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CARBON DIOXIDE REDUCTION SYSTEMS
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I. ABSTRACT

The Methoxy system for regenerating oxygen from carbon dioxide was studied. Experiments indicate that the reaction between carbon dioxide and hydrogen can be carried out with ease in an efficient manner and with excellent heat conservation. A small reactor capable of handling the CO₂ expired by three men has been built and operated.

The decomposition of methane by thermal, arc and catalytic processes was studied. Both the arc and catalytic processes gave encouraging results with over 90 percent of the methane being decomposed to carbon and hydrogen in some of the catalytic processes. Control of the carbon deposition in both the catalytic and arc processes is of great importance to prevent catalyst deactivation and short circuiting of electrical equipment.

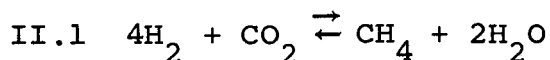
Sensitive analytical techniques have been developed for all of the components present in the reactor effluent streams.

II. INTRODUCTION

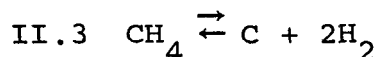
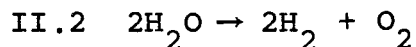
This progress report covers work done during the period 15 September 1960 to 15 March 1961. This report is concerned with further detailed experimental work carried out on the Methoxy system and some further work done on the Carboxy system.

Previous reports have discussed the general features of the Methoxy and Carboxy systems. As a brief review, a description of both systems with some of their important features and problems will be presented here.

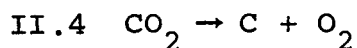
The Methoxy system is a three-step process, the first step of which involves reaction of the CO_2 with H_2 over a catalytic bed according to reaction II.1



The water formed in this reaction is electrolyzed to form hydrogen and oxygen while the methane is decomposed to carbon and hydrogen as shown in equations II.2 and II.3.



The H_2 formed in reactions II.2 and II.3 is recycled to reaction II.1 so that the net result of reactions II.1, II.2 and II.3 is



with the carbon being disposed of in some suitable fashion and the oxygen being recycled to the cabin.

Reaction II.1 is carried out over a catalytic bed and gives higher conversions at lower temperatures. In view of this, a reactor must be designed to give satisfactory conversion at a reasonable rate and in addition conserve heat for utilization in other

parts of the system. The construction and operation of such a system is discussed in Section IV of this report.

Reaction II.3, the decomposition of methane to carbon and hydrogen is of critical importance to the success of this process. Some of the problems associated with the arc process are the formation of acetylene as a by-product and the formation of carbon deposits in inconvenient locations where they can cause short-circuiting of the electrical lines. The possibility of recycling acetylene has been examined as have methods for reducing short-circuiting caused by carbon deposition. Experiments along these lines are reported on in Section V-C.

The use of hot carbon and metal rods, which is actually a catalytic process is reported in Section V-A. In these experiments some success has been achieved in depositing a relatively firm, tightly adhering carbon deposit on the rod and wire surfaces. Such a deposit would be advantageous in that the carbon could be collected in one location rather than be spread throughout the reactor.

Decomposition of methane on catalytic surfaces is discussed in Sections V-B and VD. Very efficient decomposition has been achieved and results indicate that a considerable amount of carbon can be collected on the catalyst before the catalyst becomes deactivated. The main considerations in a catalytic decomposition process are to achieve high conversions and a large ratio of carbon to catalyst before deactivation of the catalyst. Supported catalysts in which the support material is light and fluffy appear to have the best chance of fulfilling these requirements.

Further work on the direct decomposition of CO_2 in an electric arc has shown that some decomposition can be accomplished and



that the amount decomposed is dependent on the electrode material. Use of carbon electrodes appears to decrease the oxygen yield, possibly because of the reaction of CO_2 with C to form CO. Latest results, however, indicate higher decompositions than those previously achieved and indicate that further effort should be devoted to this work.



III. ANALYTICAL TECHNIQUES

Development of the Methoxy system requires many gas analyses. The key gases involved are H_2 , CH_4 , CO and CO_2 . It is also desirable to be able to detect and measure N_2 , O_2 , C_2H_6 , C_2H_4 , and C_2H_2 . An instrument designed for this service has been built and was described in an earlier report of this Laboratory.* It embodies an application of gas-solid adsorption chromatography. Its unique feature is the use of two parallel columns, one packed with silica gel and the other with Linde 5A molecular sieve. The sample is split into two fractions, one passing through each column. The molecular sieve column separates O_2 , N_2 , CH_4 , and CO . CO_2 and the C_2 hydrocarbons are so strongly adsorbed that they do not issue from the column in sharply defined narrow zones, and hence do not cause chromatographic peaks on the recorder chart. These substances are separated by the silica gel column which does not separate O_2 , N_2 , CH_4 and CO . The outputs from the two columns are combined and passed through a thermal conductivity cell. The output from the cell is a composite of the peaks of both columns.

The "retention time" of a chromatographic column for a specific substance is a function of the flow rate of the carrier gas, being shorter, the higher the rate. When two columns are used in parallel, the separation between peaks and even the order in which they appear will depend upon how the carrier gas flow is split between the two columns. With two different packings it is

* Technical Report on Carbon Dioxide Reduction Systems to National Aeronautics & Space Administration, Washington, D. C. Contract NASw-117, Period covered Sept. 15, 1959 to December 15, 1959. By Lawrence Carr & Warren Ruderman, Isomet Corporation, Palisades Park, N. J.



certain that the flow will not be the same in both. To bring this factor under control, we have inserted a needle valve at the input end of the silica gel column, through which the larger gas flow occurs. By regulating this flow we can change the peak pattern so as to avoid interferences and obtain optimum resolution.

For the study of methane dissociation the determination of hydrogen is necessary when carbon containing substances other than carbon itself are produced. An example of this is the production of acetylene by the high voltage arc. Hydrogen has the shortest retention time of any of the gases on both adsorbents. The retention times of O_2 , N_2 and CO are so nearly equal on silica gel that these gases emerge from the silica gel as a composite. The retention time of methane is also very nearly that of the composite peak gases. However, it is slightly less than the others and can sometimes be partly resolved from the others. The retention time of hydrogen is significantly less so that its peak can be resolved even from methane, though not without difficulty. Hydrogen also has a very short retention time on the molecular sieve. We have found that by adjusting the distribution of carrier gas between the two columns with the needle valve, the spacing of the two hydrogen peaks can be varied, and they can, in fact, be merged. However, this adjustment causes interference between the N_2 and CO_2 peaks. To avoid this we adjust the flow so that the hydrogen peaks are separated, with the molecular sieve peak appearing first. It is then larger than the silica gel peak, because the carrier gas flow is larger in the molecular sieve column.

A chromatogram showing a typical result for hydrogen and methane, with helium as the carrier gas is shown in Figure I A.



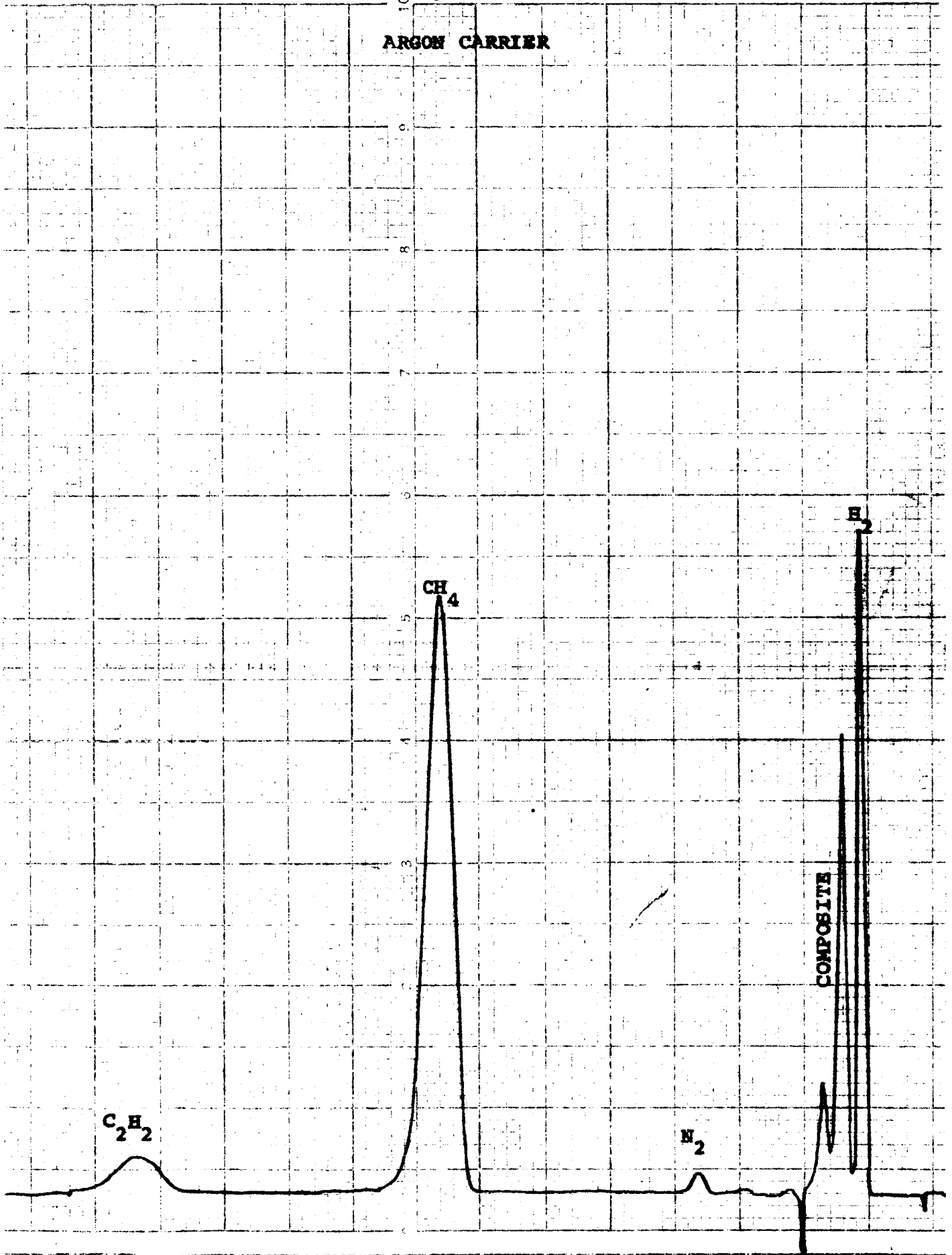
Only the sieve hydrogen peak is completely resolved. The silica gel peak is too close to the "composite" methane peak. This spacing cannot be changed by flow adjustment since both are silica gel peaks. It will also be noted that the hydrogen peaks are small. Their size could, of course, be increased by using a higher electrical sensitivity, but the sensitivity of the thermal conductivity cell for hydrogen is so small compared to that for other gases, that a sufficient sensitivity to produce good sized hydrogen peaks makes the composite peak so large that it spreads out and engulfs the hydrogen peaks.

To surmount this difficulty we have investigated the use of argon as a carrier gas. Helium and hydrogen both have high thermal conductivities while the thermal conductivities of argon and the other gases of interest are much lower. It is the difference between the conductivities of a gas and its carrier which determines the cell response. We find that substituting argon for helium as a carrier, a very large sensitivity for hydrogen results. The sensitivities of all the other gases are, of course, greatly lowered. However, since the hydrogen peaks appear first, we have found that we can increase the electrical sensitivity of the system after the composite peak appears, and obtain good chromatograms for all of the other gases except CO_2 . An example is shown in Figure I B.

Carbon dioxide is a special case. The thermal conductivity of argon and carbon dioxide are so nearly alike - 3.88 and 3.39 at 0° - that peaks useful for CO_2 determinations at low concentrations cannot be obtained. Here helium is the better carrier gas. We are presently setting up a second chromatograph for this use, which will be so adjusted as to optimize the sensitivity for CO_2 .

Figure 1B

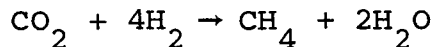
ARGON CARRIER





IV. METHANATION REACTION

Previous work on the methanation reaction has demonstrated the feasibility of carrying the reaction:

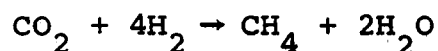


to completion in the presence of a catalyst. Further engineering development work has been carried out on this system to develop some of the operating limits and characteristics of a system of this sort.

One of the prime considerations in any oxygen recovery system for use in space vehicles is the conservation and reuse of energy. The reaction as written above is exothermic and thus there is the possibility of utilizing the heat liberated in this reaction for heating in other parts of the process. In addition, since this reaction is exothermic and since the equilibrium in the reaction is shifted to the left (lower conversion of CO_2) as the temperature increases, it is desirable to maintain the temperature as low as is consistent with a reasonable reaction rate. In a well insulated reactor which would be necessary in order to prevent heating of the space cabin, it would be difficult to maintain the temperature in the reactor at a reasonably low level ($280 - 300^\circ\text{C}$) because of the exothermic nature of the reaction, unless some auxiliary cooling method is employed. Auxiliary cooling is, however, not necessary if one uses a heat-exchanger type of reactor in which the heat liberated by the reaction is used to heat the incoming gas. In addition, the incoming gas acts to cool the reacted gases and tends to keep the temperature of the effluent gases at a reasonably low temperature thereby insuring good conversion of the CO_2 . In essence, the desired reactor would be similar to those used in a contact sulfuric acid

process plant where the incoming gases go to a relatively high temperature reactor where they are reacted rapidly but not to complete conversion, and then exchange heat with incoming gas thereby heating the incoming gas to reaction temperature and cooling the reacted gas so that when it enters the second reactor its temperature will be low enough so that complete conversion is assured, although at a slower rate in the second reactor because of the lower temperature. The exact same principle is utilized in the methane formation reactor and a diagram of the reactor which was finally built is shown in Figure 1.

It can be shown that for the reaction



approximately 50 kilocalories of heat are liberated for every mole of CO_2 reacted. From this figure and the known specific heats of carbon dioxide and hydrogen one can calculate the temperature rise of the incoming gas to be about 1300°C if all of this heat is transferred to the incoming gas. In a perfectly insulated reactor it will therefore be necessary to cool the reactor by exchanging heat with other process streams or by cooling with auxiliary cooling coils. The former alternative is more desirable since this allows better conservation of energy and eliminates need for auxiliary cooling devices.

The stages in the evolution of this reactor can be described as follows. The initial experiments were run on a glass tube reactor containing 600 grams of a ruthenium catalyst supported on alumina. The tube was heated on the outside with a heating tape. The reactor was initially brought up to 250°C with CO_2 running and then the H_2 was turned on. The temperature rose rapidly to 320°C because of the heat liberated in the reaction. In the hope that the reaction would be self sustaining, the external heat source was

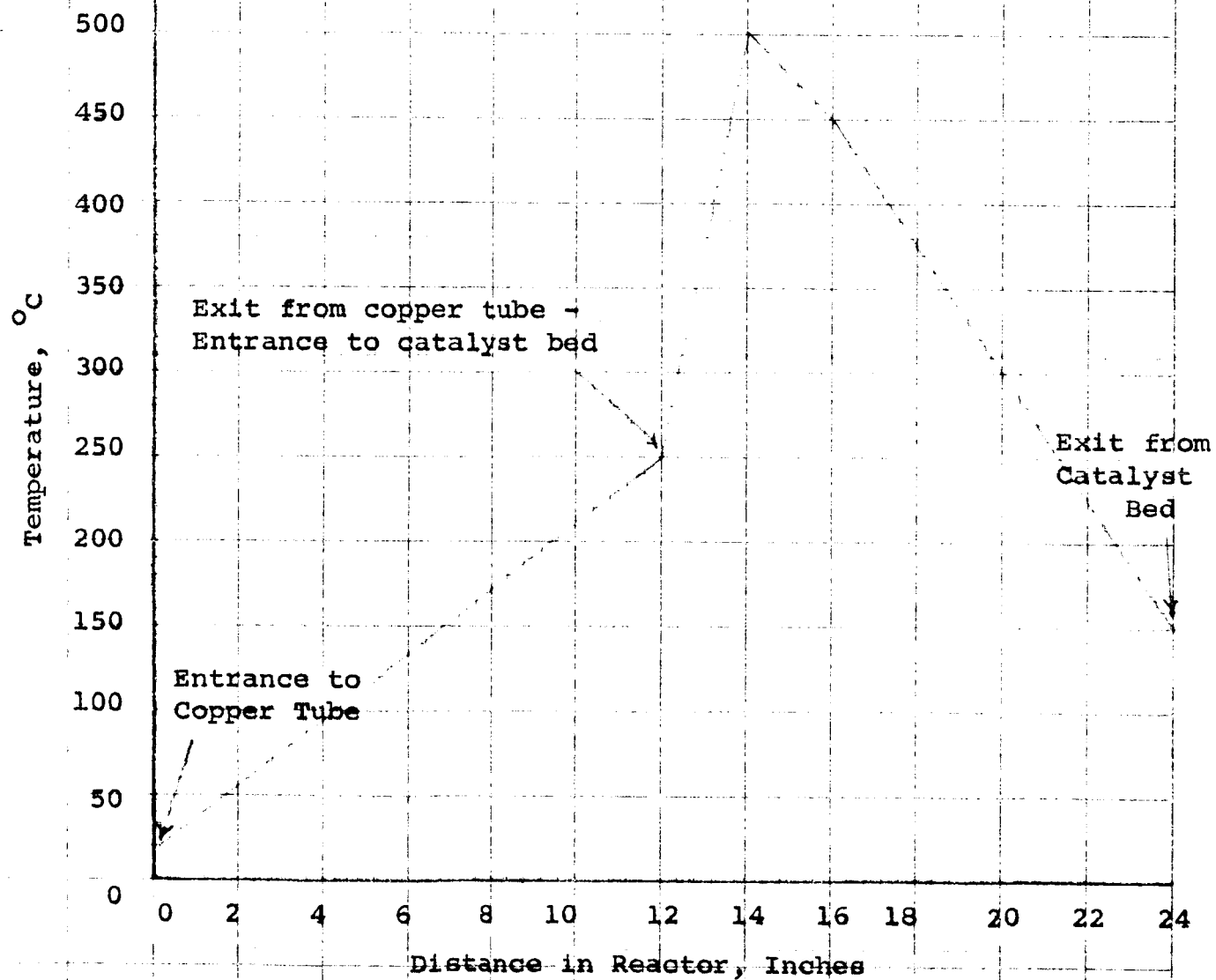


shut off. Since the reactor was not insulated in any way, the temperature soon dropped below the point where a reasonable reaction rate could be observed and the reaction ceased. During the period of operation, the water formed in the reaction was collected. Based on the amount of water collected and the feed rate of CO_2 and H_2 it appeared that the CO_2 conversion was 99 percent or better. The fact that the temperature increased when the reaction started indicated that the reaction could be self-sustaining if the reactor were properly insulated. In addition, the fact that the temperature gradient in the catalyst bed indicated that reaction was occurring in a localized zone made it appear that less catalyst was required.

Based on this consideration, a second reactor was constructed in which only 60 grams of the catalyst were used. This reactor was longer and thinner than the first in an effort to spread out the reaction zone and thus distribute the liberated heat more uniformly along the length of the reactor. Again when the reaction started, the top of the column where the reacting gas entered became very hot (about 500°C). The heating tapes were then shut off in an effort to control the reaction temperature but as soon as the tapes were shut off the reaction gradually died out and the temperature dropped. The incoming cool gas appeared to be cooling the catalyst bed thus quenching the reaction. Based on this observation, it appeared that heating of the incoming gas and cooling of the exit gas would be desirable. The incoming gas should be heated in order to prevent quenching of the reaction by cooling of the catalyst bed, while the exit gas should be cooled in order to remove the heat of reaction and bring the temperature of the exit gas down to about

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FIGURE 2
TYPICAL TEMPERATURE PROFILE IN METHANATION REACTOR



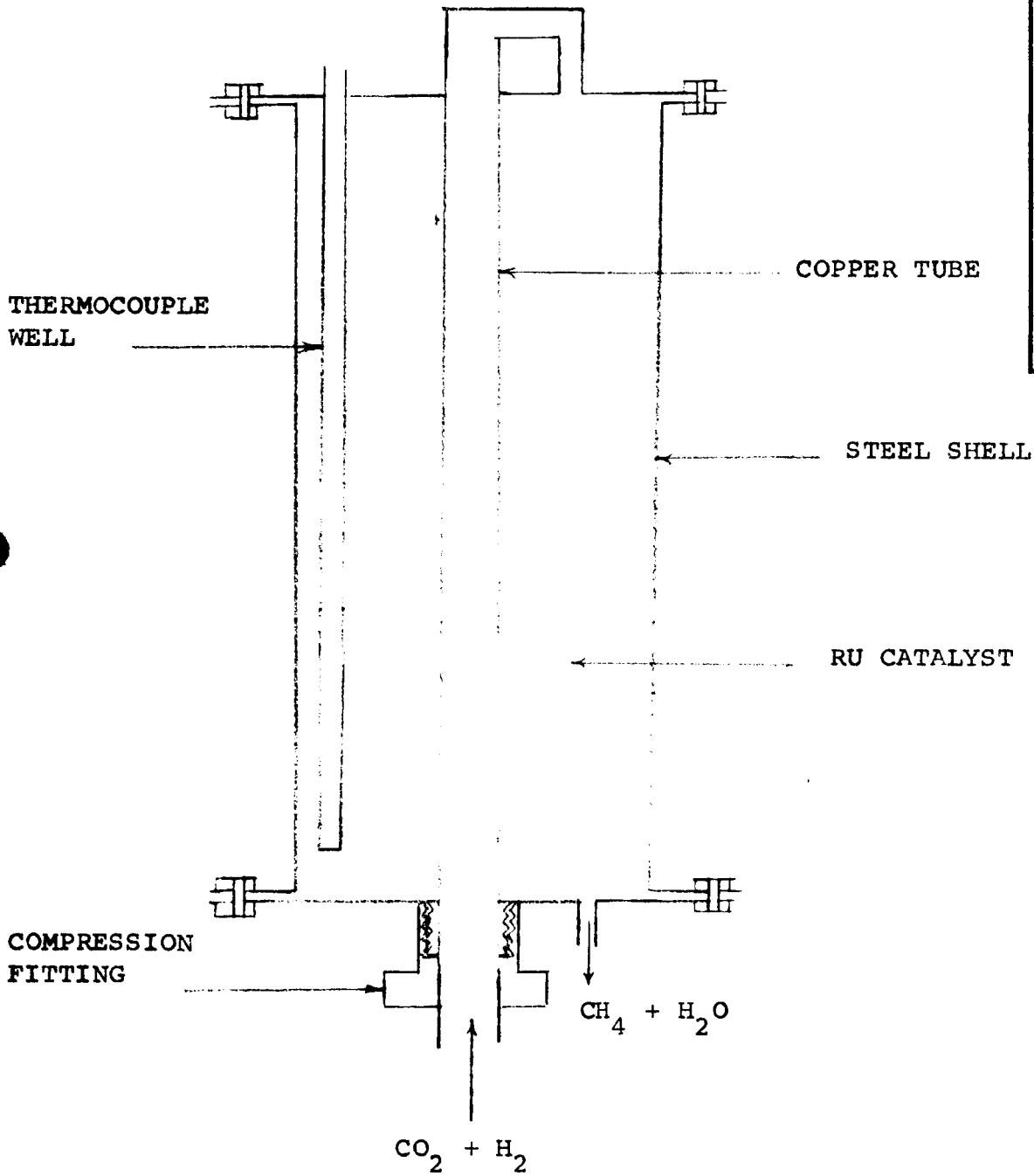


300°C where the equilibrium conversion of CO_2 is very close to 100 percent. It, therefore, appeared that a combination counter current heat-exchanger and reactor would be effective.

In this device the entering gas rises through a central copper tube that is surrounded by the catalyst. The gas rising through this tube is heated by exchanging heat with the reacting gas flowing down over the catalyst bed. In this manner, the entering gas is brought up to reaction temperature by the time it reaches the top of the catalyst bed. When it reaches the catalyst bed, it reacts rapidly liberating heat, thus causing a high temperature at the top of the catalyst bed. As the gas passes down over the catalyst bed, it is cooled by the gas coming up through the central copper tube. In this fashion the exit gas temperature is brought down to a value which gives essentially 100 percent conversion of CO_2 to CH_4 and H_2O . A typical temperature profile under operating conditions is shown in Figure 2. In a reactor containing 80 grams of the ruthenium catalyst, CO_2 , was fed in at 1500 cc/min. and H_2 at 6000 cc/min, approximately the rate for a 3-man cabin crew. The reactor was about 1 1/2 inches in diameter and a foot long exclusive of insulation. Under these conditions, water collected indicated essentially 100 percent conversion of CO_2 . These results indicate that a compact, efficient, light-weight unit capable of converting the CO_2 exhaled by 3 men to CH_4 and H_2O can be built. Future work will be directed toward determining long-term catalyst stability and the integrating of this unit into the complete Methoxy system.

Figure 1

Schematic Drawing of Methanation Reactor



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V. METHANE DECOMPOSITION

A. Decomposition of Methane on Hot Carbon Rods and Metallic Wires

The following series of experiments were undertaken to observe the character of the carbon deposit that results from the decomposition of methane on heated carbon rods and metallic wires. It was of interest to know whether some of these would yield a carbon deposit which would adhere to the rod or wire and thereby facilitate the removal of carbon from the reaction chamber. On the other hand, if the rods or wires would produce a reasonably compact but loosely adherent deposit, this would be advantageous since they could then be used continuously without removal from the reaction chamber. A mechanical means involving vibrations or scraping could be devised for periodically removing the deposit.

It is well known that methane will decompose on any surface that is sufficiently hot ($1000 - 1200^{\circ}\text{C}$). A number of catalysts promote the decomposition at significantly lower temperatures but their effectiveness in the form of metallic wires or when impregnated into carbon rods was not known. It would be desirable, for example, to find a catalytic material that would continuously diffuse to the surface of the carbon and continue to decompose more methane.

To investigate these possibilities, spectrographic carbon rods were impregnated with salts of a number of metals, namely, Fe, Ni, Co, Cr, Zn, and Cu. The following metallic wires were also prepared for similar experiments: nickel, iron, steel, stainless steel, nichrome, monel, tungsten, platinum, etc. Thus far, only a few of these materials have been studied.

1. Apparatus - Since it was desirable to observe the nature of the carbon deposit during the decomposition of the methane, a large Vycor tube (4" in O.D., 18" long, 3520 cc volume)



was used in a laboratory set-up illustrated in Figure 3. Supports were provided for the rods or wires so that they could be electrically heated with the aid of a step-down transformer and a variable autotransformer (Powerstat). Unfortunately no means was available for measuring the temperature of the rods or wires other than visual observation of their color.

After evacuation of the chamber, methane was admitted through a rotameter flowmeter. Silicone seals were provided in the entrance and exit lines so that gaseous samples could be obtained in a hypodermic syringe for analysis with a gas chromatograph. These analyses, combined with visual observations and weights of the carbon deposit, permitted an evaluation of the extent of decomposition.

2. Results and Discussion - Carbon Rods. Before studying the impregnated carbon rods, data were obtained on the behavior of a spectrographically pure carbon rod (1/8" x 12"). These results are summarized in Table I. At temperatures below 650-700°C the conversion of methane to carbon and hydrogen or other products is small. The extent of the conversion increases rapidly with increase in temperature until at 65 amperes (800 - 850°C) 52% of the 116 cc/min of entering methane was decomposed. Although the fraction of methane converted decreased with increasing flow rate, the volume of methane decomposed increased. Thus, at a flow of 116 cc/min or an average residence time of 30.5 min. the volume of methane converted was 60 cc/min. At a flow rate of 500 cc/min or a residence time of 7.1 min, the volume converted was 150 cc/min. Apparently the rate of conversion in this apparatus is limited in part by mixing and diffusion.

At the higher temperatures significant quantities of products other than carbon and hydrogen were formed. This was evidenced by a brown deposit and an oily film that formed on the Vycor tube. White crystals of a product with an odor similar to

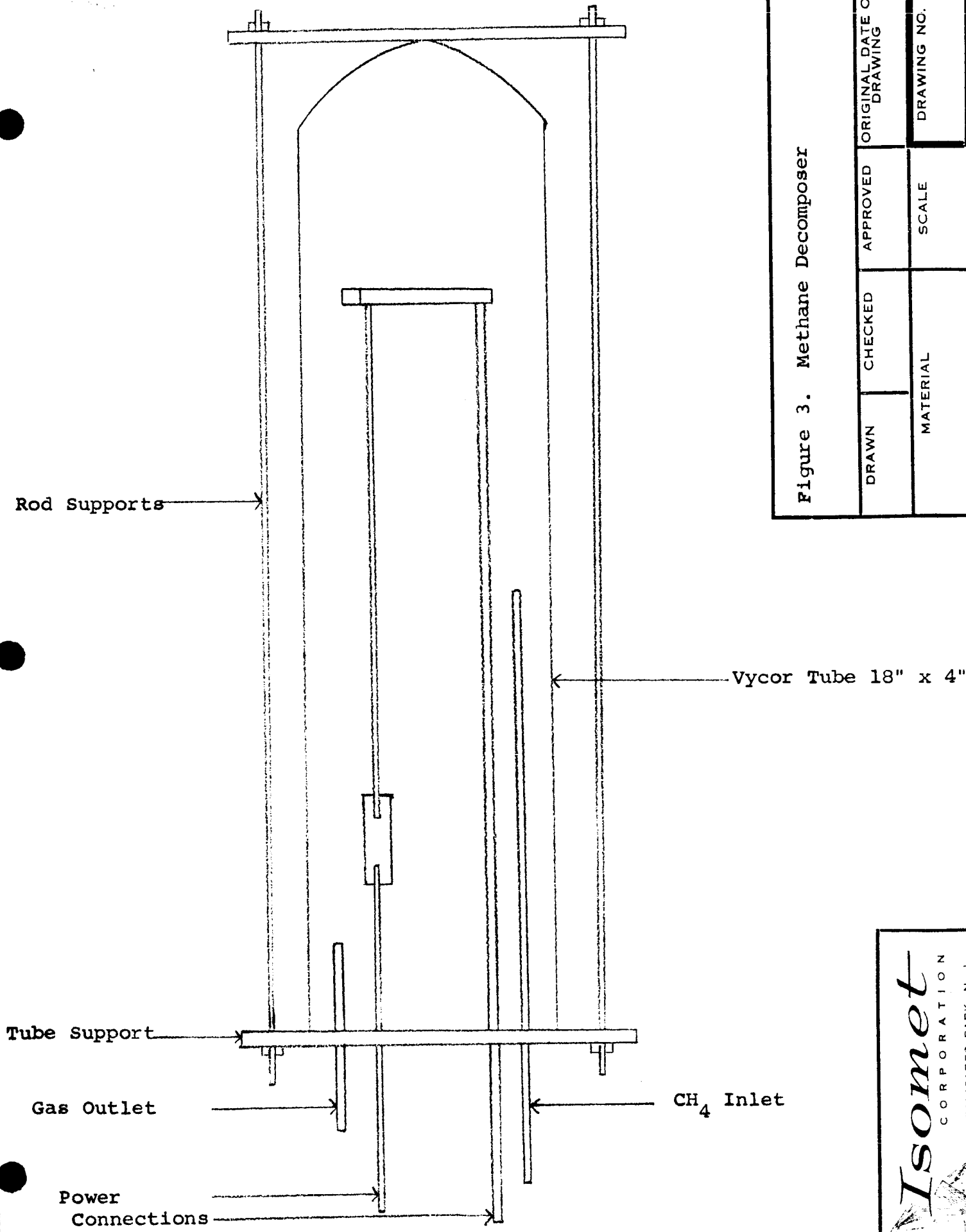


Figure 3. Methane Decomposer

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TABLE 1 - SPECTROGRAPHIC CARBON ROD (1/8" x 12")

<u>CH₄</u> <u>(CC/MIN.)</u>	<u>% CH₄</u> <u>CONVERTED</u>	<u>CH₄ CONVERTED</u> <u>(CC/MIN.)</u>	<u>AMPS</u> <u>_____</u>	<u>APPROX.</u> <u>TEMP. (°C)</u>
116	5	6	42	650-700
116	14	17	49	700-750
116	40	46	60	750-800
116	52	60	65	800-850
192	46	88	65	800-850
500	30	150	65	800-850



that of naphthalene were also deposited in the exit tube.

The weight of carbon deposited on the rod after about 7 hours of operation was 1.5 g. This was a hard, graphitic deposit that could not be removed. The surface was covered with many stiff whiskers of carbon, all pointing upward. In addition to the carbon deposited on the rod, an appreciable quantity of less dense carbon formed on the battery clip used for the electrical connection at the top of the carbon rod. Later experiments on similar battery clips in a heated quartz tube indicated that this carbon probably resulted from the decomposition of the side products. A heavy graphite connector was used in subsequent experiments.

3. Impregnated Carbon Rods. Spectrographic carbon rods are sufficiently porous that they may be impregnated with solutions. This was accomplished by first evacuating a tube containing the carbon rod and then admitting a solution of the nitrate of the desired metal as, for example, $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (15 g/30 cc of solution). Approximately 0.6 ml of each solution was taken up by the individual rods. The rods were air dried and then oven-dried at 120°C . Final decomposition of the nitrate salts was accomplished in the Vycor tube by heating the rods before the start of a particular run.

The data summarized in Table 2 illustrate the conversions obtained as a function of the current heating the rods. A comparison of the data for these rods with those for the pure carbon rod indicates that impregnation with Fe, Co or Ni did not improve the conversion. In fact, the extent of conversion with the pure carbon rod seemed to be greater for the same current. The data found in Table 2 might have resulted from small changes in the geometry and the electrical connections to the rods which may have changed



TABLE 2 - IMPREGNATED SPECTROGRAPHIC CARBON RODS
(1/4" x 12", 4 G.)

<u>FILA- MENT</u>	<u>CH₄ (CC/MIN.)</u>	<u>% CH₄ CONVERTED</u>	<u>CH₄ CONVERTED (CC/MIN.)</u>	<u>AMPS</u>	<u>C DEPOSIT (g.)</u>	<u>AMT. OF METAL (g)</u>
C Rod + Fe	192	2	4	40	0.7	0.2
	192	5	10	50		
	192	5	10	55		
	192	10	19	60		
	192	25	48	65		
	192	33	63	70		
C Rod + Ni	192	3	6	40	0.7	0.3
	192	4	8	50		
	192	4	8	55		
	192	5	10	60		
	192	10	19	65		
	192	19	36	70		
C Rod + Co	192	2	4	40	0.7	0.3
	192	3	6	50		
	192	4	8	55		
	192	5	10	60		
	192	18	35	65		
	192	27	52	70		



the convection of gases in the tube as well as the temperature of the rod.

Although the conversions of methane for the three impregnated rods were not greatly different, those for the rod impregnated with iron are somewhat higher. We can conclude from these preliminary results that no advantage is achieved by impregnation of the carbon with either Fe, Ni or Co. Apparently the carbon deposited on the rod limits the metal's participation in the conversion of the methane.

As with the pure carbon rod, side products were formed when the current was about 60 to 65 amperes. These products collected in a brown deposit on the Vycor tube and finally as an oil film and crystals at the lower end of the tube. The carbon deposit on the rod was hard and graphitic with many small carbon whiskers.

Since the carbon deposited on the rods is dense and therefore occupies a small volume, a methane decomposition system based on this behavior could have some advantages. It would facilitate the handling of the carbon although its dense form might limit its later use as an adsorbent. The side products could be eliminated readily by providing the reaction tube with a short section of an active supported catalyst. Most of the carbon from the methane would deposit on the carbon rods in the form of a parallel grid, and the carbon from the small quantity of side products would be deposited on the supported catalyst. A system such as this will be tested in later experiments.

4. Metal Wires. Although solid metal wires have a relatively small catalytic surface, they sometimes show significant



catalytic activity. This may arise from the diffusion or the transport of metal during chemical reaction or from the formation of intermediates such as carbides or hydrides with the appropriate stability. As mentioned previously, wires of a number of metals were obtained for these experiments. However, only the iron and nickel wires have been studied thus far.

These were mounted between the electrodes in the apparatus illustrated in Figure 3 and data were taken as described for the carbon rods. The results are summarized in Table 3. Significant differences were observed between the behavior of the iron and nickel wires. The carbon deposit on the iron was loosely held and could be removed readily while the carbon on the nickel was hard and graphitic. Furthermore, the iron wire developed hot spots, became brittle, and finally failed at a current of about 50 amperes. Apparently the iron forms a carbide which has different catalytic properties. Further experiments are planned in which the iron wires will be tested in a combustion tube furnace.

In order to determine the effect of increasing the metallic surface, a 1/4" wide strip of filter cloth made of 0.009" nickel wires was used (Multi-Metal Wire Cloth Co. No. XXD400). This width was selected so that the weight of the strip was approximately the same as the weight of the nickel wire previously used. At about the same temperature, the conversion of methane was about double that for the nickel wire. However, the extent of conversion did not increase in proportion to the surface area. After a short time of operation, the surface became covered with a grey carbon deposit similar to that obtained on the carbon rods.



TABLE 3 - METAL WIRES (12" LENGTH)

<u>Filament</u>	<u>CH₄ (cc/min.)</u>	<u>% CH₄ Converted</u>	<u>CH₄ Converted (cc/min.)</u>	<u>Amps</u>	<u>Approx. Temp. (°C)</u>	<u>Carbon Deposit</u>
Fe wire (0.056")	192	3	6	40	--	--
	192	5	10	50	--	Loosely held
Fe wire looped (0.056")	192	2	4	40	--	Loosely held
	192	5	10	45	--	
Ni wire (0.064")	192	3	6	66	800-850	Compact
	192	7	13	75	900-950	
	102	20	20	75	900-950	
Ni wire cloth	192	32	37	65	900-950	
(XXD-400-0.037" x 1/4")	102	39	40	67	900-950	Grey, Graphitic



In all cases, side products were obtained when the temperature was sufficiently high for significant conversions. Thus, the use of such wires would require a reaction system similar to that proposed for the carbon rods.

B. Experiments on Supported Nickel Catalysts

1. Commercial Nickel Catalyst. During some preliminary experiments wherein the relative catalytic activity of a variety of materials was studied, it was noted that a number of supported nickel catalysts were relatively effective for the decomposition of methane at temperatures from 600-700⁰C. These survey experiments were run in a 25 mm quartz tube heated with a combustion furnace. From 6 to 9 materials could be placed at intervals in small quartz boats for comparison of their activity under essentially the same conditions. Of special interest were the supported nickel hydrogenation catalysts such as Girdler's G60, as well as nickel nitrate decomposed on such supports as MgO, ZrO₂, asbestos, quartz wool or fibrous aluminum silicate. Decomposition of methane when passed over these catalysts occurred at relatively low temperatures with considerable increase in catalyst volume. It was observed that the G60 catalyst, as well as the MgO and ZrO₂ disintegrated and appeared to be dispersed throughout the carbon that formed.

Since a small quantity of catalyst appeared to produce a rather large quantity of carbon, further experiments were carried out in the apparatus shown in Figure 3. We were particularly interested in determining the quantity of carbon that could be produced per gram of catalyst. The change in activity



with dispersion of the catalyst in the carbon was also of interest.

For the first experiment (Table 4) a piece of 100 mesh stainless steel wire screen 3" wide and 11" long was rolled into the form of a 5 mm i.d. tube and then spot-welded. This was filled with ten 1/4" pellets (3.4 g) of the nickel hydrogenation catalyst (G60). The ends of the tube were clamped between the electrodes for heating by an electrical current. When the wire screen was dull red (about 600^o-650^oC) about 37% of the 192 cc/min or 71 cc per min. of methane was decomposed. After about one hour the screen started to swell and burst. Within 2 hours the screen had split open along its full length. During this time 5.3 g of carbon had formed, most of which adhered to the screen in reasonably compact form. The experiment had to be terminated before the maximum quantity of carbon was produced.

In order to determine the total quantity of carbon that a given quantity of catalyst would produce, a crucible was used in the apparatus shown in Figure 3. It was supported and heated in a coil of B & S No. 14 Kanthal resistance wire. One pellet of G-60 catalyst (320 mg) was cracked into smaller pieces and placed on the bottom of the crucible. The temperature inside the crucible, as determined with a thermocouple, was slowly increased from 580 to 666^oC. over a period of 9 hours. During this time the crucible became full of carbon and some fell out over the sides. The weight of carbon produced was 5.1 g which represents a ratio of carbon to catalyst of about 16. When the experiment was stopped, about 10 cc of methane was being decomposed per min. at 660^oC compared with a maximum conversion of 35 cc at the same temperature. Thus, the catalyst was still reasonably



TABLE 4 - NICKEL HYDROGENATION CATALYST (GIRDLER - G60)

Catalyst Mounting	Apparatus Used	CH ₄ (cc/min.)	% CH ₄ Converted	CH ₄ Converted (cc/min.)	Temp. (°C)	C deposit (g.)	Catalyst (g.)	Ratio of Carbon to Catalyst
In S. S. Tube of 100 mesh	Vycor Tube	192	37	71	650	5.3	3.4	1.5
In crucible	Vycor Tube	192	11	21	617	5.1	0.32	16
		102	18	18	621			
		192	18	35	659			
On Quartz Fiber	Combustion Furnace	192	39	75	638	14	1.0	14



active after it had formed carbon equal to 16 times its own weight. No side products were observed during this experiment.

Catalysts of the type used in this experiment are essentially consumed since it would be difficult to recover them for re-use. However, they would be useful if the conversion per gram of catalyst could be made sufficiently high. Since about 290 g of carbon are in the carbon dioxide expired by one man per day, a ratio of 16 to 1 for carbon to catalyst corresponds to about 18 g of catalyst per man per day. If this ratio could be increased to 100 to 1 instead of 16 to 1, only 2.9 grams of catalyst would be required per man per day or about 260 g (0.6 pound) for 30 days with a three-man crew. This would probably represent an acceptable loss.

Further experiments are in progress on this as well as other catalysts to determine the maximum carbon production per gram of catalyst without appreciable loss in activity. Another important consideration is the bulk density of the carbon. It would be desirable to have it greater than the 0.4 g/cc obtained in the above experiment.

2. Nickel Catalyst on Quartz Fiber. The experiment just discussed suggested the use of a loosely packed catalyst support such as quartz fiber. This would allow space for the deposition of a considerable quantity of carbon and aid in its removal from the reaction tube. It would also allow its use as an absorbent for air purification.

A preliminary experiment was tried in which 1 g of the G60 nickel hydrogenation catalyst was dispersed as a fine powder on 2.8 g of quartz fiber. This mixture was then put into a 25 mm quartz tube and heated with a combustion furnace. In order to



reduce the possibility of plugging, the methane was introduced throughout the 10" length of the catalyst by means of a distributor tube. This was a 3/16" stainless steel tube drilled with 1/16" holes and then wrapped with a 100 mesh stainless steel screen. Although such an arrangement prevents plugging it reduces the contact time of the methane that passes through the system. The system is being remodeled to improve its operation in this respect.

As listed in Table 4, the extent of methane conversion was 39% of 192 cc/min or 75 cc/min at 638°C. Unfortunately the furnace was accidentally heated to 800-900°C and apparently sintered the catalyst since the activity was appreciably lower when the temperature was returned to 650°C. The run was continued with slowly increasing temperature from 700 to 900°C. Although the decomposition of methane was still progressing, the experiment was stopped to repeat it at lower temperatures. The weight of carbon produced was 14 g or a ratio of carbon to nickel catalyst of 14 to 1. Additional experiments are planned wherein the nickel catalyst is to be deposited directly on fibers of quartz, asbestos and aluminum silicate by decomposition of nickel nitrate.

The above system shows some promise if the metal catalyst can be supported on a loose fibrous structure that allows considerable space for carbon deposition. It is not known yet whether higher ratios of carbon to catalyst can be achieved while still maintaining sufficient activity.

C. Electric Arc Decomposition of Methane

An alternate route for the decomposition of methane to produce carbon and hydrogen is the one wherein methane is passed



through an electric arc. Previous experimental efforts have indicated the feasibility of this process. Due, however, to the fluffy character of the carbon that forms in this process and the tendency for it to produce short-circuiting problems, a clear understanding of the nature of the reaction has been lacking. The series of experiments discussed below indicate the progress made in elucidating this reaction since our last report.

1. Apparatus: The power supply consisted of an A. C. Luminous Tube transformer with an output of 15,000 volts at 30 milliamperes. A Triplet Model 660 A. C. - D. C. Wattmeter measured the power supplied to the arc.

Numerous reaction vessels, usually of Kimax glass to permit visual observations, were employed. Inside of these, the electrodes, gas inlet and outlet tubes were mounted. To minimize the possibility that the electrode material might affect the course of the methane conversion, spectroscopically pure graphite electrodes were usually employed. However, electrodes made of aluminum and molybdenum were also utilized. In all instances, the electrodes were eroded by the arc at their high points. The connecting tubing utilized for the gas streams was usually made of Pyrex glass and Tygon or rubber tubing.

In an effort to reduce the short-circuiting problem, the electrodes were rotated in several experiments. In these instances, the electrodes were connected through lucite insulating couplings to either a Bodine Electric Company 1725RPM Stirrer or a 23 RPM KGI Stirrer. The use of these stirrers, particularly at the higher rotation rates, prevented a complete short from developing between the electrodes.



The electrode materials were mounted on stainless steel shafts which carried the electrical load. To prevent the carbon that was formed from short-circuiting to the shafts, they were enclosed in pyrex tubing of slightly larger diameter than the shafts. Nonetheless, carbon did accumulate on the protective tubing during the course of the run and produce shorting problems. The rest of the equipment used in these experiments was of the customary laboratory variety and will not be further detailed. A sketch of the reaction vessel is shown in Figure 4.

2. Analytical Procedure. The gas chromatographic arrangement discussed in Section III was utilized when analyses of the gas streams were desired. One cc samples of both the entering and exiting gas streams were taken and injected into the gas chromatograph. A comparison of the chromatographs obtained prior to the start of the arc enabled us to know when the reaction system was purged of air. When gas mixtures were passed into the reaction tube, the percent concentrations of the components were also determined by gas chromatographic analyses.

Preliminary analyses of the products of the decomposition reaction indicated that the major gaseous components were hydrogen, undecomposed methane and acetylene. A small amount of ethane and nitrogen was also detected. However, this was present initially in the technical methane utilized in these experiments and remained unchanged during the course of any particular experiment.

Accordingly, the gas chromatograph was calibrated for the expected gaseous products. Pure samples of varying amounts of hydrogen, methane and acetylene were injected into the chromatograph. A comparison of the chromatographs for these samples indicated that

To Stirrer or Support

Transformer connection

C + H₂ Outlet Tube

Methane Inlet Tube

S.S. Electrode holder

Spectroscopically Pure Graphite

12" x 3" Kimax Reaction Tube

S.S. Shaft

Pyrex Insulating Tube

Rubber stopper

Transformer Connection

Shaftbushing

To Stirrer or Support

Figure 4. Methane Electric Arc Decomposer

DRAWN		CHECKED	APPROVED	ORIGINAL DATE OF DRAWING
MATERIAL			SCALE	DRAWING NO.

Isomet
CORPORATION
PALISADES PARK, N. J.



a linear relationship existed between the peak heights observed and the concentration of the gas that was present. Graphs were prepared from these data and utilized to determine the percent composition of the exiting gas stream which contained the gaseous products of the reaction.

Inasmuch as no additional products other than carbon were detected, the amount of carbon that should, in theory, be produced could be calculated by simple procedures. This permitted a comparison of the theoretical amount with the experimentally determined amount obtained by weighing. In turn, the agreement found between the two values validated the theory that only carbon, hydrogen and acetylene were produced.

A dry-ice trap installed in the system between the exiting gas stream and the gas sampling point prevented the contamination of the gas chromatograph with moisture or other possible condensable by-products when samples were taken for analysis. Frequent examinations of this trap indicated the absence of such products.

3. Results. A number of preliminary experiments were run which enabled us to establish our procedures and operating conditions for the runs reported below. Parameters studied were the effect of various configurations of the reaction vessel, the effect of flow of methane through the electrodes (copper tubing was used in these experiments), the effect of rotation of the electrodes, the effect of scraping devices made of lucite or steel and the effect of application of a magnetic field to concentrate or to spread the arc.

The laboratory set-up that proved most useful for our purposes is illustrated by Figure 4. This consisted of a 12"



Kimas glass pipe, 3" in diameter (1.39 l.). This permitted us to make any desired adjustments or replacements readily. In addition, the progress of the reaction could be visually observed.

The data in Table 5 represent experiments wherein methane was passed into the arc between rotating electrodes. The first column describes an experiment wherein the power input was kept as low as possible. This was done to observe the efficiency of the conversion reaction and the nature of the carbon that was formed at these conditions.

It is evident from the data that at low power inputs, most of the entering methane remains unreacted. However, with increased power supplied to the arc, more of the methane is converted. The total conversion of methane, for example, increased from 2.3% at 10 watts to 11.8% at 105 watts. This efficiency is not very striking especially since part of the conversion was to acetylene. The fluctuations apparent in the data arise from the sampling technique. While the efficiency of the arc varied during a particular time interval, the sample that was taken at the end of that period represented an average value and not the instantaneous composition. The mixing and diffusion of the gases within the reaction tube produce an average mixture which may vary from minute to minute.

During the course of the run, it was necessary to increase the electrode distance to prevent the carbon whiskers that developed on the electrodes from shorting. A major portion of the carbon that was produced formed in this manner. Rotation of the electrodes caused the whiskers to break and fall off the electrodes at frequent intervals. However, during the growth of these whiskers, the



TABLE 5 - ROTATING ELECTRODES

Experiment	1						2		3	
CH ₄ (cc/min.)	150						150		150	
Direction of flow	Up						Up		Up	
Pressure	Atm.						Atm.		Atm.	
Electrode Shape	Pointed Cylinder						Pointed Cylinder		Pointed Cylinder	
Electrode Material	Graphite						Graphite		Graphite	
Electrode dist. (")	1/8 - 5/8						1/4 - 7/8		1/2	
Arc duration (min.)	160						33		55	
Watts	10	20	30	60	105	60	130	130-140		
% Composition of exiting stream:										
H ₂	4.5	9.4	9.9	22.6	20.2	10.4	45.3	47.4		
CH ₄	95.5	88.6	89.6	74.9	78.8	88.1	46.5	44.1		
C ₂ H ₂	0	2	0.5	2.9	1.0	1.5	8.2	8.5		
% CH ₄ converted to:										
C ₂ H ₂	0	4.3	1.1	6.8	2.2	3.2	22.4	23.6		
C ₂ H ₄	2.3	1.8	4.4	5.2	9.6	3.2	14.2	15.3		
% CH ₄ converted										
total:	2.3	6.1	5.5	12.0	11.8	6.4	36.6	38.9		
C appearance	Compact						Fluffy		Fluffy	
C calculated (g.)	0.62						0.27		0.56	
C found (g.)	0.44						0.26		0.41	



electrode distance decreased and the power dropped. Consequently, the amount of methane that was decomposed also decreased. A complete short-circuit was prevented by having the electrodes rotate but the conversion efficiency was poor.

An important result of this experiment, it should be noted, was the nature of the carbon that was formed. Unlike subsequent experiments, the carbon was compact and accumulated in the bottom of the reaction tube during the course of the run. If the formation of carbon could be controlled to yield such a form continuously and the decomposition efficiency could be improved, then this form of carbon would lend itself to easy removal from the reaction tube. Also, shorting difficulties which occur at places other than between the electrodes would be minimized. Further attempts in this direction will be made.

The second column represents an experiment which was similar to the one discussed above. In this instance, however, the incoming methane was directed through the arc and the power input was higher. At 60 watts, this experiment showed a slightly poorer result. It is possible that equilibrium conditions had not been reached within the reaction tube when the sample was taken. At 130 watts, however, the change in the percent composition of the exiting gas stream is quite apparent. With increasing power input, the efficiency of the conversion reaction improves. The percent of methane converted increased from 6.4% at 60 watts to 36.6% at 130 watts. Acetylene formation also rose rapidly increasing from 3.2 to 22.4%. Of the total methane converted at 130 watts 61% of it was converted to acetylene. This was a sharp increase over the acetylene formation noted in the first experiment. Apparently, the greater the power supplied to the arc, the greater is the amount of acetylene that is produced.



The carbon that was formed was fluffy and rapidly filled the reaction tube. Very little developed on the electrodes except when the power input was low. However, whiskers did grow at all time during the run and reduced the conversion efficiency. At the higher power input, the whiskers appeared to break from the electrodes more readily.

In the last example, a manually controlled glass rod was inserted between the electrodes. It was possible by manipulating this rod to break off the whiskers and thereby improve the arc. However, this improved the arc only temporarily since the carbon whiskers quickly reformed and reduced the efficiency.

Once again, the carbon was fluffy in nature. The analyses of the exiting gas stream compared favorably with the experiment previously discussed for a power input of 130-140 watts. The percent of methane converted was 38.9% which checked the 36.6% found in experiment 2. As mentioned earlier, the comparison between the calculated and observed carbon was quite good for all three runs. This confirmed the earlier identification studies which indicated the products of the reaction would be hydrogen, carbon and acetylene.

To improve the arc and possibly reduce the carbon whisker problem on the electrodes, a 500 mmf capacitor was placed in parallel with the Luminous Tube Transformer. This helped to concentrate the arc. Table 6 illustrates the data that was obtained when this arrangement was utilized.

Comparing Tables 5 and 6 for the same flowrate of 150 cc/min. of methane, we note that the fraction of methane converted increased from 38.9% to 59 - 70%. This represents approximately 50 percent increase in the conversion efficiency. While the formation of



TABLE 6 - CONCENTRATED ARC

CH ₄ (cc/min.)	150	150	450	* 75
Arc duration (min.)	75	125	33	72
% Composition of exiting stream:				
H ₂	58.4	66.2	45.8	39.1
CH ₄	25.9	17.5	42.9	52.2
C ₂ H ₂	15.7	16.3	11.3	8.7
% CH ₄ converted to:				
C ₂ H ₂	49.9	55.5	31.6	22.9
C	9.1	14.8	8.4	8.5
% CH ₄ converted total	59.0	70.3	40.0	31.4
Direction of CH ₄ flow	Down			
Pressure	Atm.			
Electrode shape	Pointed Cylinder			
Electrode Material	Spectroscopic graphite			
Electrode Separation (inches)	1/4			
Electrode Rotation	None			
C found (g.)	1.74			
C calculated (g.)	2.89			
Watts	Approximately 190			
C appearance	Fluffy			

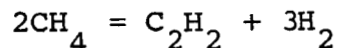
* Efficiency decreased due to shorting difficulties



carbon was about the same, the major factor in the improved efficiency was the increase in the conversion to acetylene. This increased from 23.6% to an average value of 53%.

Inasmuch as there was no shorting between the electrodes, most of the energy of the arc was utilized in decomposing methane. When the flowrate of the incoming methane was increased to 450 cc/min., the total fraction of methane converted dropped to 40%. This is approximately the fractional conversion found at 150 cc/min. when no capacitor was utilized. Therefore, at a flowrate of 450 cc/min, it would appear to be possible to take care of a man's requirements for oxygen in a closed environment if 3 such reactors were employed in the Methoxy system. These reactors would convert the methane to carbon, hydrogen and acetylene. At 450 cc/min. or 27 l/hr. 1.1 moles of CO_2 expired by a man could be converted to oxygen and carbon as carbon and acetylene.

Acetylene formation may be represented by the following equation:



This equation indicates that 3/4 of the hydrogen present in the methane can be recovered and can be reused in the Methoxy process. From the above results, if 1/4 of the hydrogen initially supplied for the methane formation reaction could be replenished from a stored supply, then these results indicate the electric arc might be a major component of the Methoxy system. The acetylene produced could be discarded or possibly recycled. The latter possibility is discussed below.

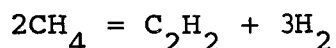
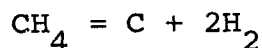
The last column of Table 6 indicates the results obtained when the flowrate was decreased to 75 cc/min. By this time, the carbon within the reaction tube had built up to such an extent



that it was beginning to create shorting problems. Part of the energy supplied to the arc was being wasted and instead of an improvement being found in the conversion efficiency a decrease to 31.4% was observed.

Concentrating the arc by using the capacitor clearly improved the conversion efficiency. The decrease in the efficiency observed at 450 cc/min. as compared to 150 cc/min was due to the decrease in residence time in the reaction tube that resulted from the higher flow rate. Carbon within the tube was again fluffy and quickly filled the tube. The disagreement in the two carbon values listed probably is due to the fact that the calculated value assumes the flowrate to be constant. Actually, this fluctuated and no doubt caused appreciable error in the calculations that were made.

If we assume the following reactions as being the only ones that occur in the electric arc process:



then the above data can be explained. With acetylene being formed in the quantities discussed above, it is obvious that its concentration will gradually build-up once it is separated from the hydrogen and recycled with the methane to the reaction tube. Therefore, it was desirable to discover what effect acetylene would have on the conversion efficiency if it were present in the incoming gas stream.

Hence, some experiments were carried out wherein synthetic mixtures of methane and acetylene were passed into the reaction tube. Table 7 illustrates the data obtained when such experiments



TABLE 7 - CH₄ - C₂H₂ MIXTURES - CONCENTRATED ARC

Experiment	1	2	3
CH ₄ + C ₂ H ₂ (cc/min.)	450	150	150
Direction of gas flow	Down	Down	Up
Pressure	Atm.	Atm.	Atm.
Electrode shape	Pointed Cylinder	Pointed Cylinder	Pointed cylinder
Electrode material - Spectroscopic Graphite		Spectroscopic Graphite	Spectroscopic Graphite
Electrode dist. (")	1/4	1/4	1/4
Entering mixture: % CH ₄	82.6	65	47.5
% C ₂ H ₂	17.4	35	52.5
Watts	190	190	190
C found (g.)	1.14	1.49	0.57
C calculated (g.)	3.78	1.65	0.31
C appearance	Fluffy	Fluffy	Fluffy
Arc duration (min)-7	35 25 19	13 24 29 10	13
% Composition of exiting stream:			
H ₂	39.2 48.1 51.9 54.8	47 61 43 54	41
CH ₄	40.2 31.7 27.9 25.9	22 12 28 18	20
C ₂ H ₂	20.6 20.2 20.2 19.3	31 27 29 28	39
% CH ₄ converted to:			
C ₂ H ₂	18.9 19.7 21.4 12.0	0 0 0 0	0
C ₂ H ₂	17.0 26.3 29.4 40.0	52.1 76.8 50.7 66.4	73.4
% CH ₄ converted total:			
	35.9 46.0 50.8 52.0	52.1 76.8 50.7 66.4	73.4

Electrodes not rotated. Acetylene dried prior to entry into reaction tube.



were run. In experiment 1, for example, a mixture which contained 82.6% methane and 17.4% acetylene was passed through the arc which was again concentrated by means of the capacitor. The analyses of the gas samples taken during the run indicated the conversion of methane to be increasing up to a maximum of 52%. Carbon formation from the methane, likewise, increased and at the end of the experiment represented 77% of the total conversion. The formation of acetylene from methane, on the other hand, appears to remain fairly constant, until near the end of the run when it decreased. This might indicate that the concentration of acetylene in the reaction tube had reached a limit which was beginning to suppress further acetylene formation. Unfortunately, the arc shorted at that time and the run was discontinued.

The comparison of the two carbon values is poor and again underlines the problem of comparing instantaneous results with average conditions of the reactions system. Fluctuations in the conversion calculations are also present and arise from this problem.

It is apparent, however, that the presence of acetylene in this run was not detrimental and was instead beginning to drive the conversion reaction in the direction of forming carbon only. Carbon formation increased rapidly at the end. Comparing this data with Table 6 for a flowrate of 450 cc/min. indicates what the differences were in the conversions. Carbon formation in this instance rose to 40% as compared to the previously observed 8.4% of Table 6. Decomposition of the acetylene in the mixture did not appear to take place.

In the second experiment, the flowrate of the gas mixture was reduced to 150 cc/min. This is one-third the flowrate that



would be required by a man per day to recover oxygen from carbon dioxide in the Methoxy system. A gas mixture of 65% methane and 35% acetylene was utilized. The agreement, in this run between the calculated and observed carbon is quite good. Again, the carbon formed was fluffy in nature.

The important point to note from the data is that the acetylene, 35% of the incoming gas stream, remained unreacted and drove the methane conversion reaction only in the direction of forming carbon. This indicates that recycling of acetylene is possible in this system and that once a steady state is reached between 17 - 35% acetylene, no further acetylene should be formed. Hence, the conversion to carbon is vastly improved. Also, the conversion of methane to carbon was between 50 - 75% at all times. Comparing these data with that of Table 6 indicates how well the total conversions agree and how much increase there was in the carbon formation, namely, from 14.8% to 50% or better.

A gas mixture containing 52.5% acetylene and 47.5% methane was studied in the third experiment. Again, the carbon formed was fluffy and quickly caused problems. There was no conversion of methane to acetylene as was expected from the previous run. The percent of methane converted to carbon was 73.4. With improved apparatus wherein the carbon that is formed is removed, the conversion efficiency should be even better than thus far observed. Again, the added acetylene, even though it represented 52.5% of the mixture, remained unreacted in the arc.

As indicated above, further work with improved designs is to be undertaken. The indications are that once a steady state of acetylene concentration is reached, conversion of methane will only be in the direction of carbon formation. Therefore, the

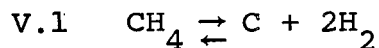


separation of hydrogen from acetylene mixtures will have to be examined. It is possible that acetylene might be simply converted by another step in the process.

However, since it is not detrimental to converting methane, its presence can be tolerated. Therefore, the major objective of future work with the electric arc as with the other decomposition procedures will be to overcome the carbon removal problem.

D. Pyrolysis of Methane

1. Introduction. Methane at atmospheric temperature is a highly stable substance. At more elevated temperatures the endothermic dissociation reaction occurs:



From available free energy data the equilibrium dissociation can be computed over a wide range of temperatures. At equilibrium, methane is 10% dissociated at 360°C and 70 % at 790°C.

At temperatures up to about 1100°C dissociation appears to be a surface reaction. The carbon formed generally adheres strongly enough to the hot surface to make its removal difficult without suspending operation. At high temperatures, such as those produced by the electric arc, carbon is often produced in a finely divided form which is carried from the reaction zone by the off gas stream, from which it may be recovered by filtration, centrifugal action or electrical precipitation.

Disposal of the carbon is a major problem in the development of any closed circuit respiratory system. In the Methoxy system, if the lower temperature surface reaction is used either a method of removing the carbon from the hot surface during operation must be developed, or else reactors must be removed from



service periodically and cleaned. To provide continuous service at least two reactors will be required in a system so designed that one can be emptied while the other is in service. At higher temperatures it may be possible to develop a reactor which can be operated continuously. However, the removal of carbon from the gas stream requires additional equipment with which operational problems must be anticipated. The relative merits of the two approaches can be assessed only by experimental study.

In this section of the report we present the results of studies of the dissociation of methane on several surfaces.

2. Apparatus for Low Temperature Pyrolysis. Pyrolysis experiments were performed in ceramic or "Vycor" tubes heated in tube furnaces. Two furnaces were used, and will be designated as "small" and "large". The small furnace was a laboratory combustion furnace, the heating shell of which was split in half longitudinally. The two halves are joined by a ring, which allows the furnace to be opened for quick cooling and easy insertion of a reactor tube. It is 13 in. long and will accommodate tubes up to 1 1/4 in. o.d. It has a Nichrome winding and can be operated up to 1000°C. The "large" furnace cannot be opened. It is 18" long and will accommodate tubes up to 2 1/2" o.d. It has a Kanthal winding and can be operated up to 1200°C.

Flow rates were measured with flowmeters of the floating ball type. These were calibrated for the various gases used with the formulas and graphs furnished by the manufacturer. Temperature was measured with chromel-alumel thermocouples and a Rubicon thermocouple potentiometer. In some experiments the total amount of methane fed was measured with a wet test meter.



In all experiments the feed gas was Matheson Company's "Technical Grade" methane, 90.0% minimum purity. The principal impurities as shown by chromatographic analysis were ethane and nitrogen. All analyses were made with the chromatograph described in another section.

3. Pyrolysis in an Empty Tube. Using the small furnace a run was made in a 3/4 in. i.d. "Vycor" silica tube with a 1/4 in. carbon rod lying along the bottom in order to see if carbon was preferentially deposited on either surface. The volume of the hot zone was estimated to be 70 cc. A constant feed rate of 50 cc/min. or 43 V/V/hr. (volume fed per hour divided by the volume of the hot zone) was maintained. A plot of the conversions observed in the temperature range 750^o-1000^oC is shown in Figure 5.

Also shown in Figure 5 are the results obtained in an empty 1 3/4 in. "Zircum" refractory tube in the large furnace. Here the temperature was held between 1112^o and 1126^oC and the flow rate varied over the range 11.5 - 57.6 V/V/hr. These data fall in a closely spaced group and show no correlation with flow rate, indicating that changes in flow rate of this magnitude change the conversion by too small an amount to override the random error.

In both experiments carbon deposited in the form of a hard scale over the entire hot surface. It showed no significant preference for either of the surfaces offered. It separated spontaneously from the smooth "Vycor" surface upon cooling. It clung more tenaciously to the rougher surfaces of the other refractories, but could be fairly easily scraped away. 22.3 g of carbon were collected from inside the large tube.



These results show the possibility of a methane decomposition system large enough to sustain one man based on an open tube of about the size used in the larger furnace at 1100 to 1200°C. One gram mole of methane must be dissociated per hour. The hot zone of this tube has a volume of about 600 cc. To decompose 1 gram mole of methane per hour with 65% conversion requires a feed rate of 38 liters/hr. of methane or 63.4 V/V/hr. The highest feed rate used to obtain the data in Figure 5 was 50 V/V/hr. However, the small effect of feed rate found over the range studied and the large effect of temperature indicate that this rate of dissociation can probably be reached below 1200°C. To operate the large furnace in this temperature range requires 900 - 950 watts. A properly designed vacuum furnace should consume considerably less power.

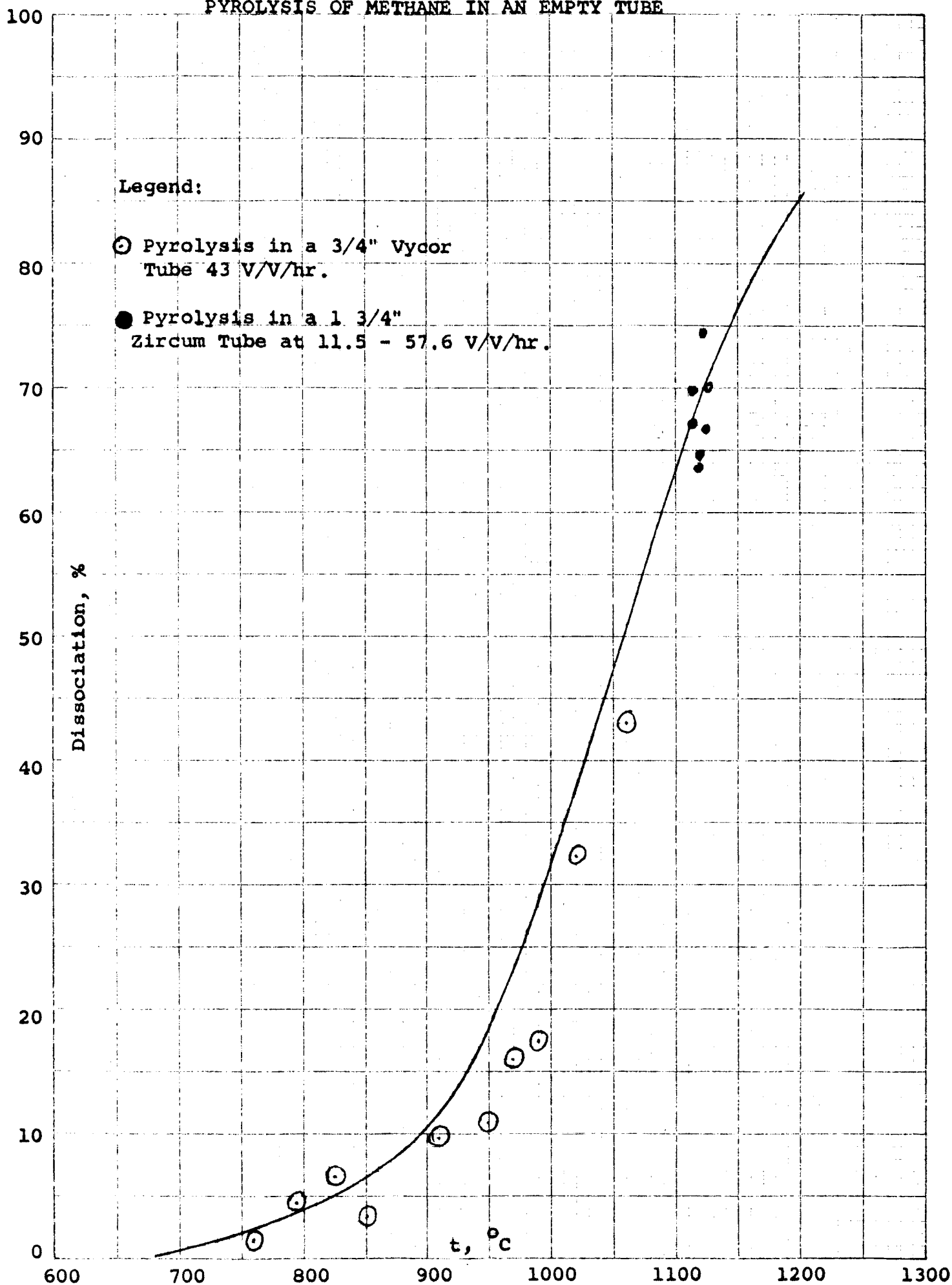
4. Pyrolysis in a Carbon Packed Tube. The rates of surface reactions usually are significantly higher when a large contact area is available. This condition is met when the gases are passed through a tube containing a granular packing with large specific surface through which the gas can flow readily. With the methane dissociation reaction any surface must rapidly be coated with carbon and become effectively a carbon surface. Carbon packings are therefore of primary interest.

It will be recognized that the use of packing will further complicate the carbon removal problem. However, it may be possible to design a system which will continuously remove granules from the bed, reduce them in size, and then return them thus achieving continuous removal of the carbon.

Several such packings have been studied experimentally. The results shown in Figure 6 were obtained with activated.

FIGURE 5

PYROLYSIS OF METHANE IN AN EMPTY TUBE





cocoonut charcoal. This well know adsorbent charcoal has a large specific surface and a rather small internal volume. If a large surface will promote the methane dissociation this packing would be expected to cause a high dissociation when fresh, but to deteriorate rapidly as the pores fill with carbon. This is seen to be the case. The experiment was performed in the small furnace at 1000°C and 50 cc/min. (43 V/V/hr.) feed rate. Dissociation over the first half hour of operation was 97%. After that it decreased very rapidly and after 4 hours appeared to be leveling off at about 30%.

A packing of briquetted wood charcoal was studied in the large furnace. The briquettes were crushed, fines sifted out rejected and $1/4"$ to $1/8"$ granules selected. Tube and thermowell were weighed and 720 CC of this material was charged. It was heated in a stream of nitrogen until water and pyrolytic substances were no longer evolved. After cooling the tube and contents were weighed and the bed weight found to be 153 g. It was heated again in a stream of nitrogen until no CO could be detected. Methane was then fed. Throughout this run methane was fed through a wet test meter. After leaving the meter the gas was dried over silica gel before entering the reactor.

Plots of the conversion obtained as a function of temperature at 200 cc/min. and 400 cc/min. - 16.7 and 33.3 V/V/hr. - are shown in Figures 7 and 8.

After cooling, the tube and contents were again weighed. The weight of carbon deposited in the bed was 115 g. The bed at the end of the run was 43% by weight deposited carbon. The duration of the run was 35.6 hours. A total of 30.8 cu. ft. of

FIGURE 6
PYROLYSIS OF METHANE OVER ACTIVATED COCOANUT
CHARCOAL AT 1000°C, 43 V/V/HR.

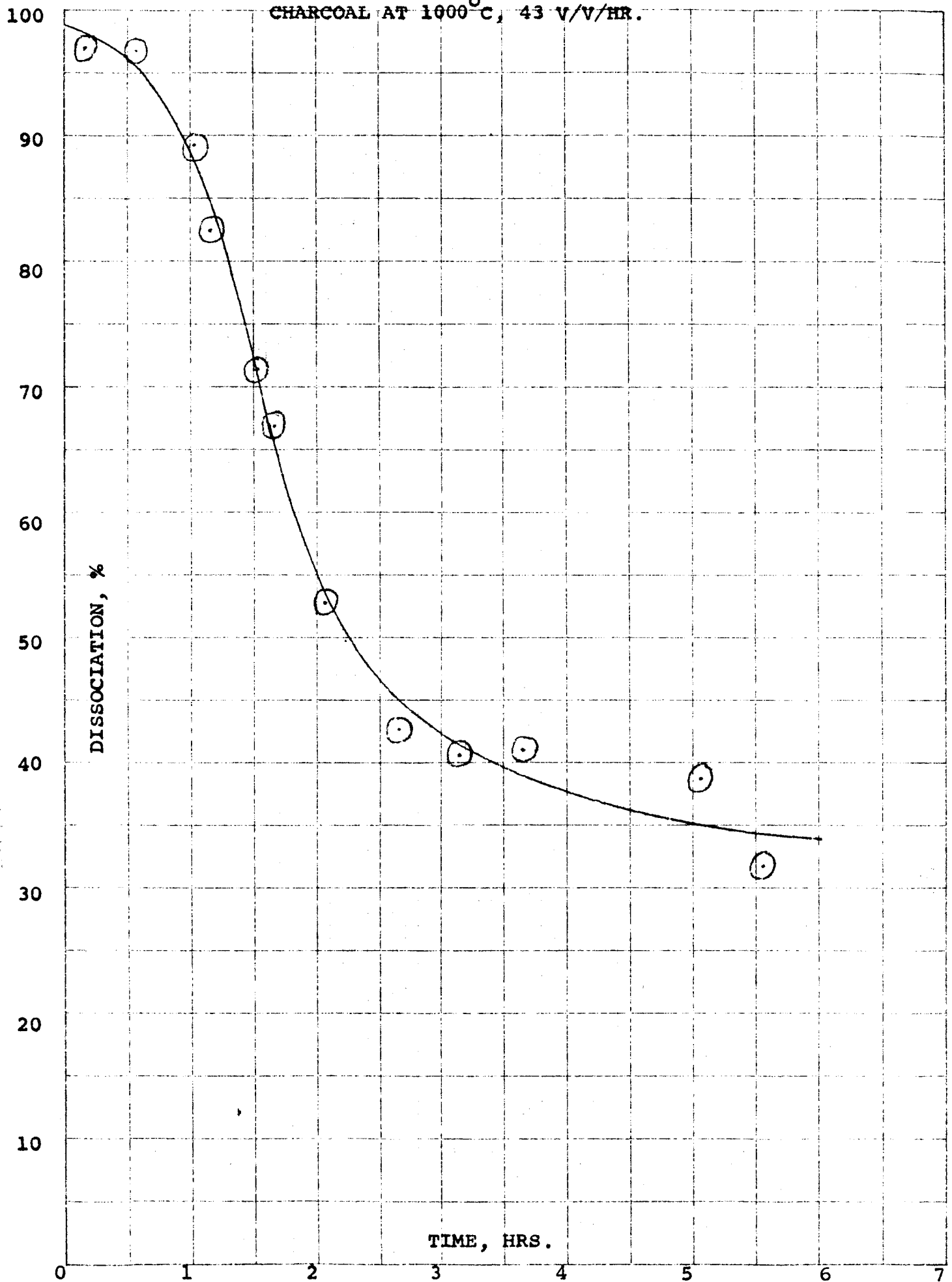


FIGURE 7
PYROLYSIS OF METHANE OVER BRIQUETTED WOOD
CHARCOAL AT 16.7 V/V/HR.
Broken curve is the equilibrium dissociation

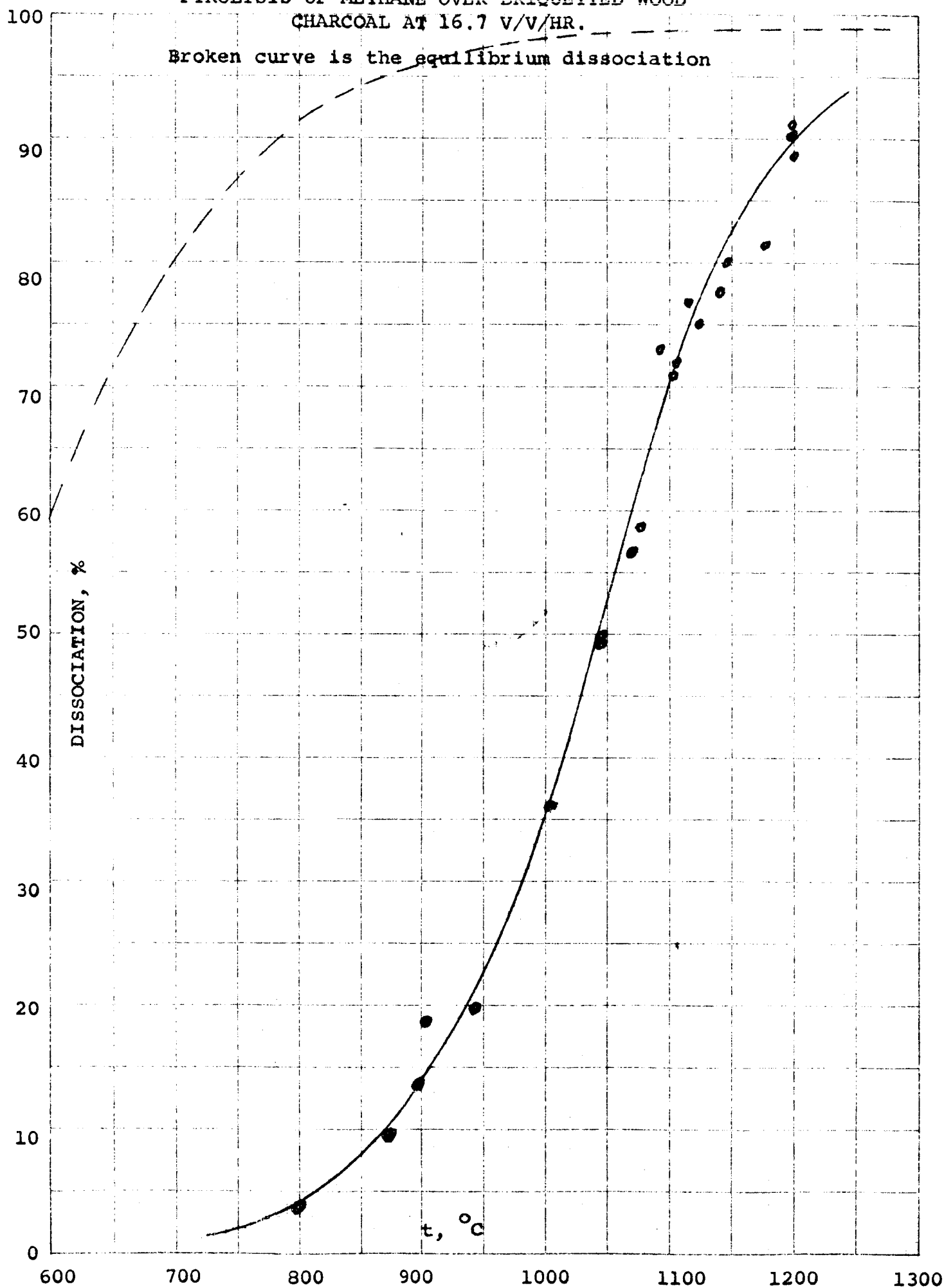


FIGURE 8
 PYROLYSIS OF METHANE OVER BRIQUETTED WOOD
 CHARCOAL AT 33.3 V/V/HR.

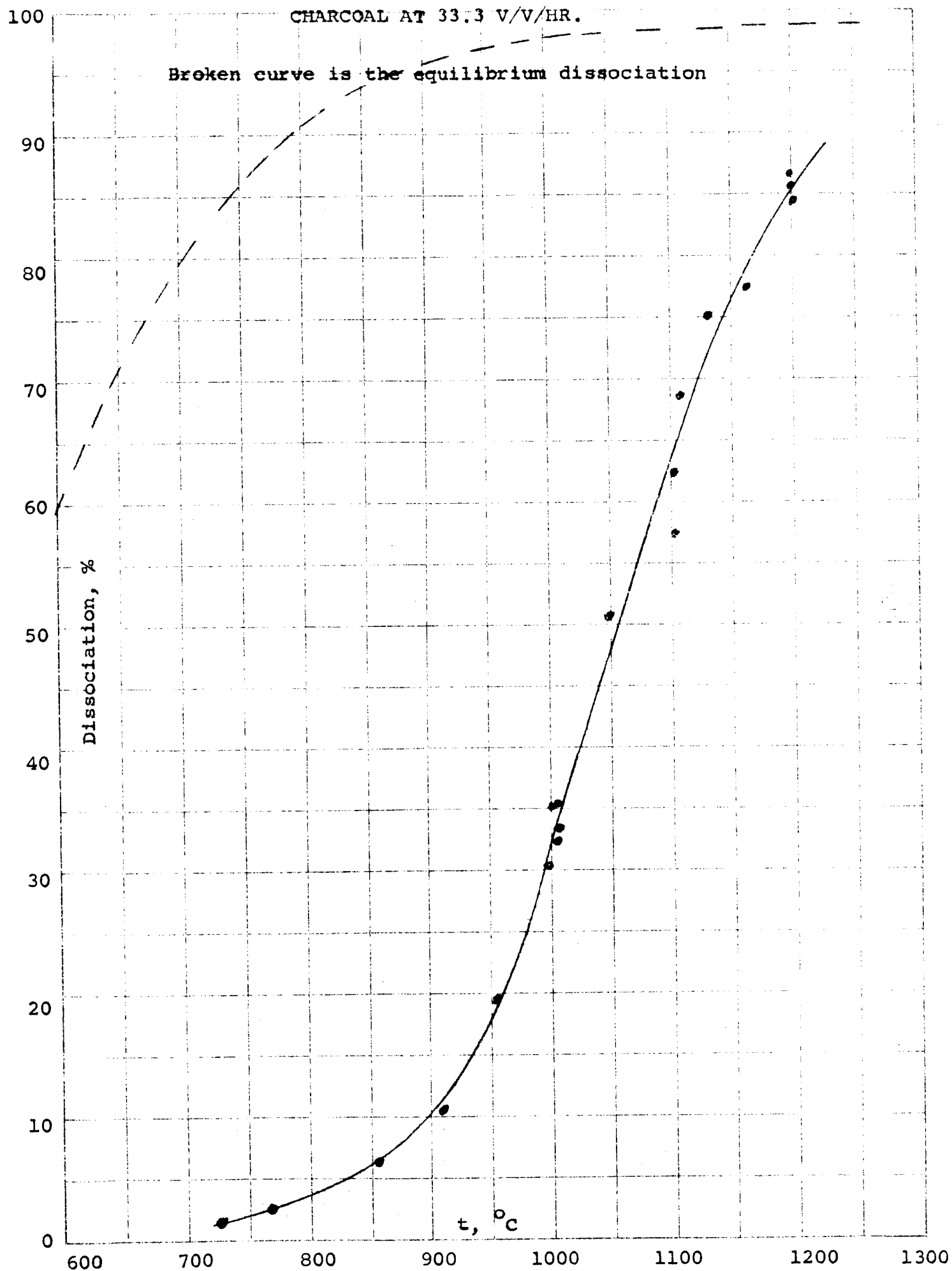


FIGURE 9
PYROLYSIS OVER LOW SURFACE CARBON PACKINGS

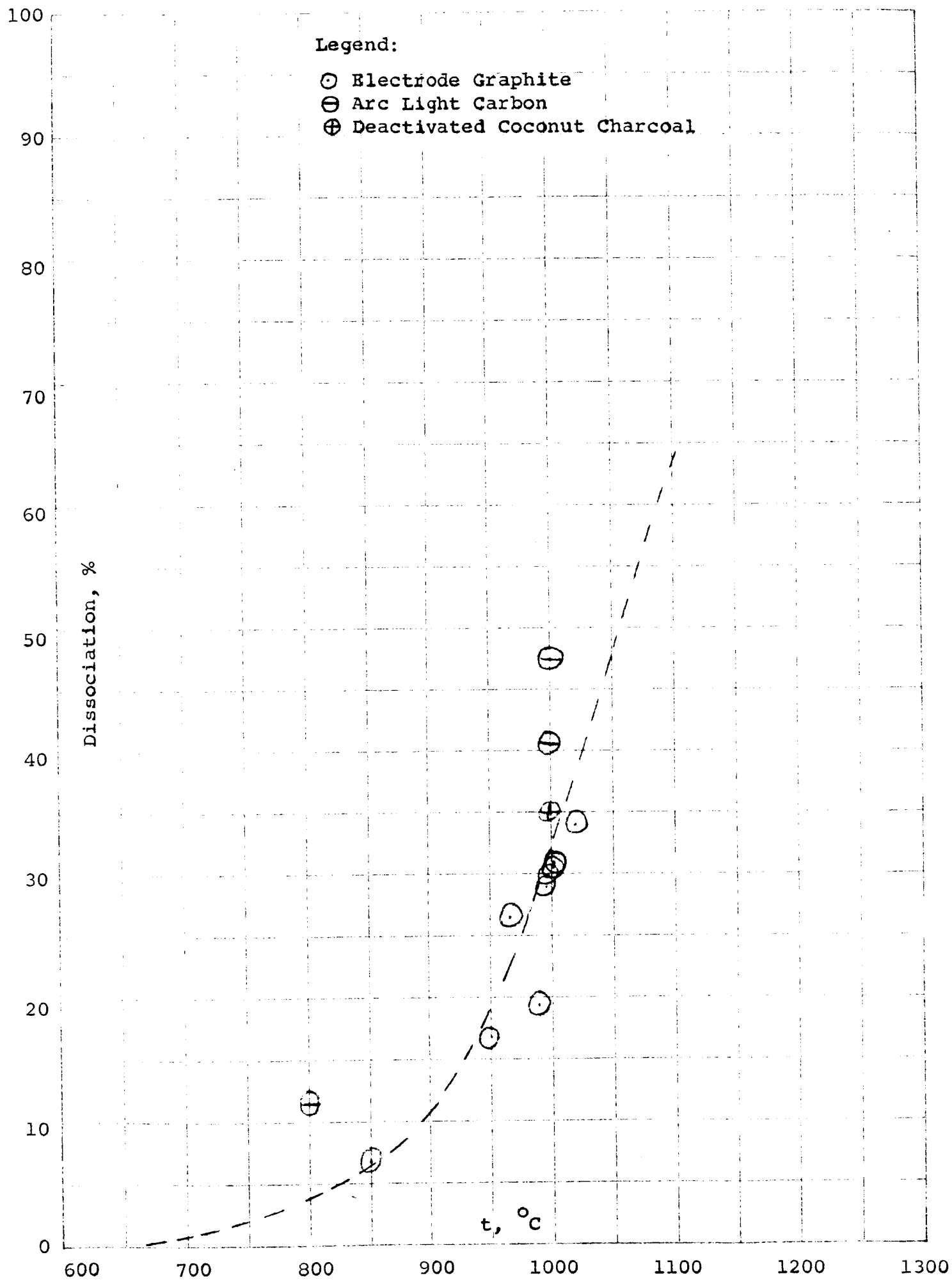


FIGURE 10
PYROLYSIS OVER CYANAMID AEROCATALYST NR-1

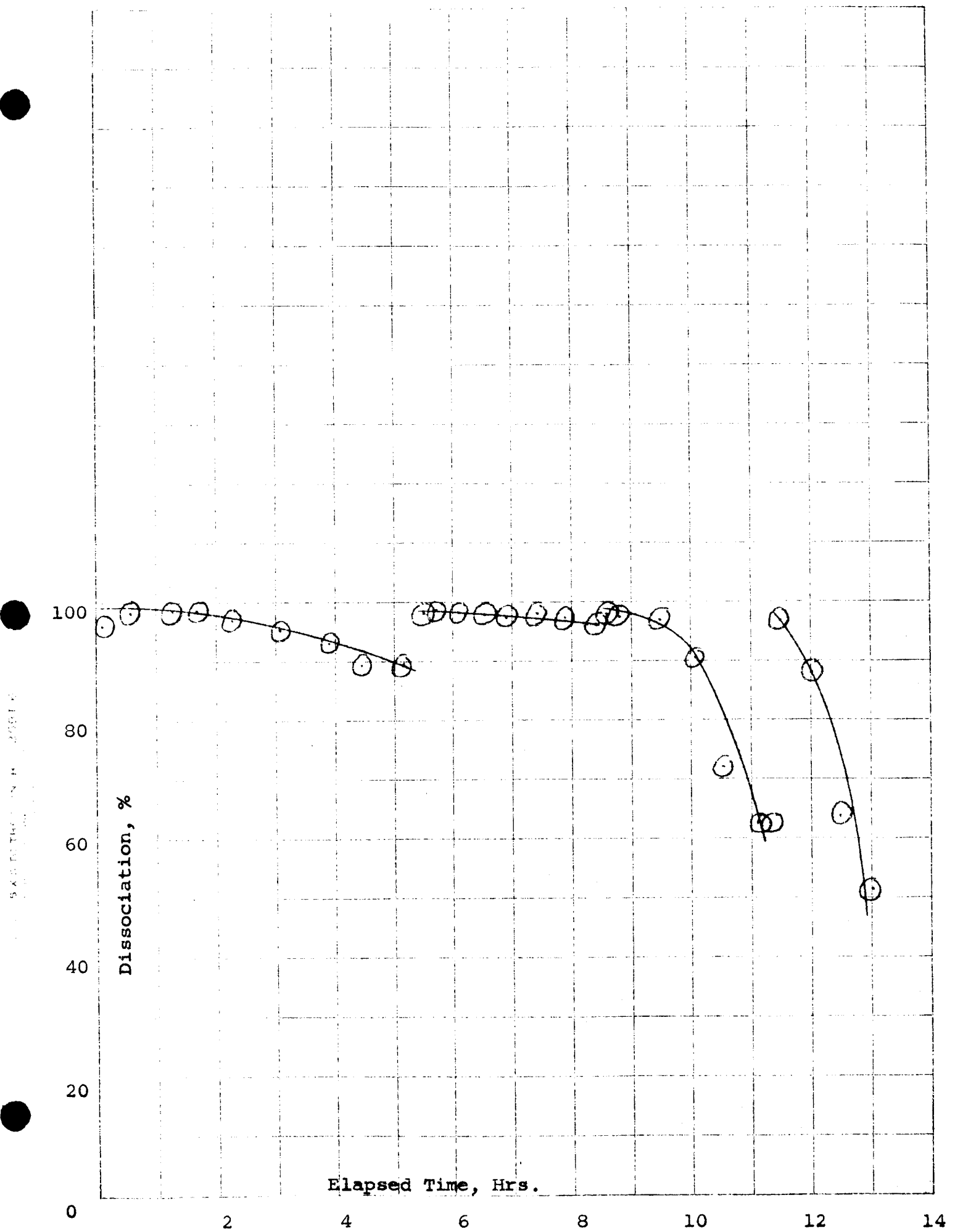


FIGURE 11
 PYROLYSIS OF METHANE OVER GIRDLER G-3A CATALYST

Legend:

○ 17 V/V/Hr.

⊖ 34 V/V/Hr.

Broken curve is equilibrium
 dissociation

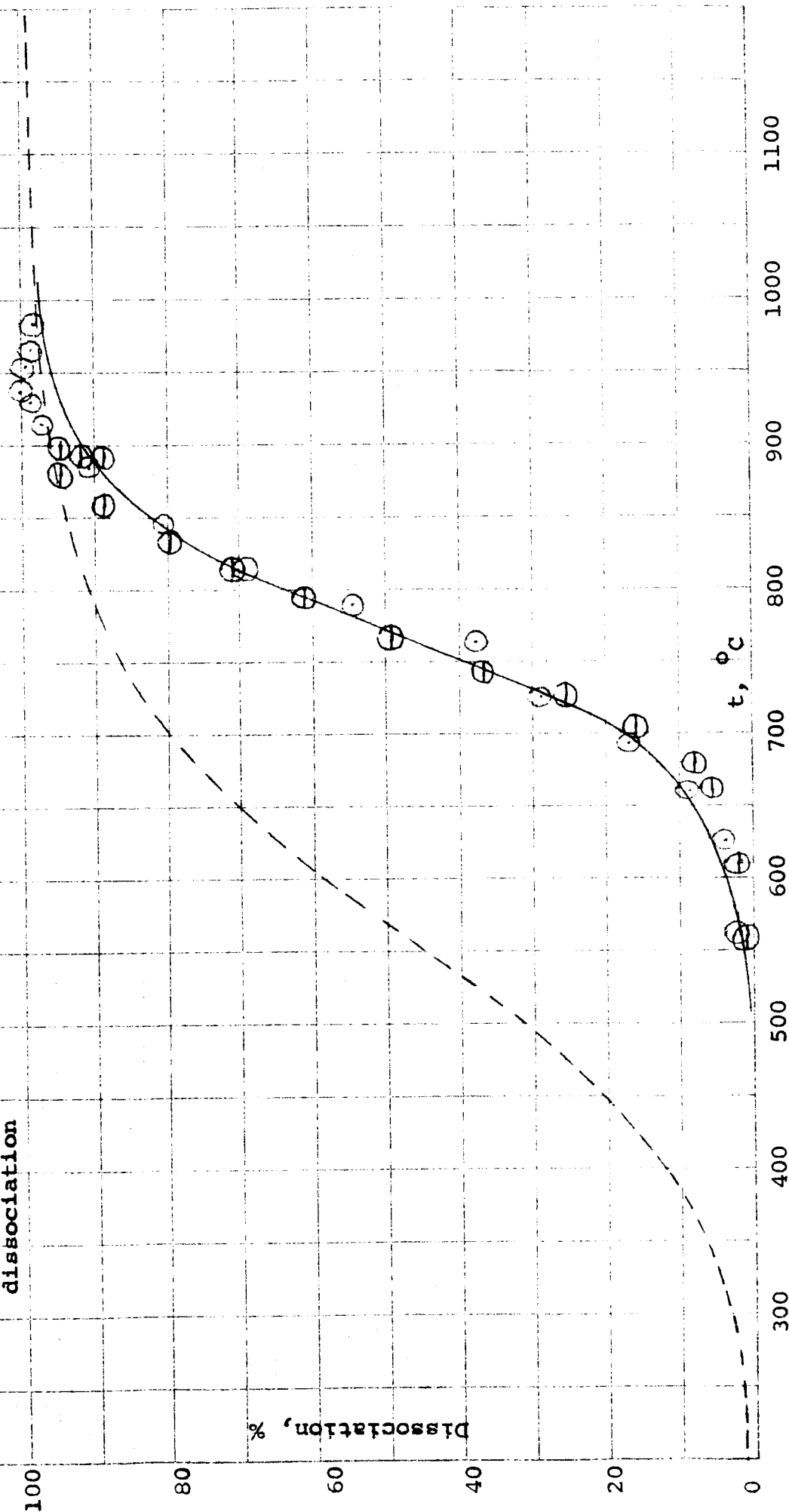


Figure 1A

HELIUM CARRIER

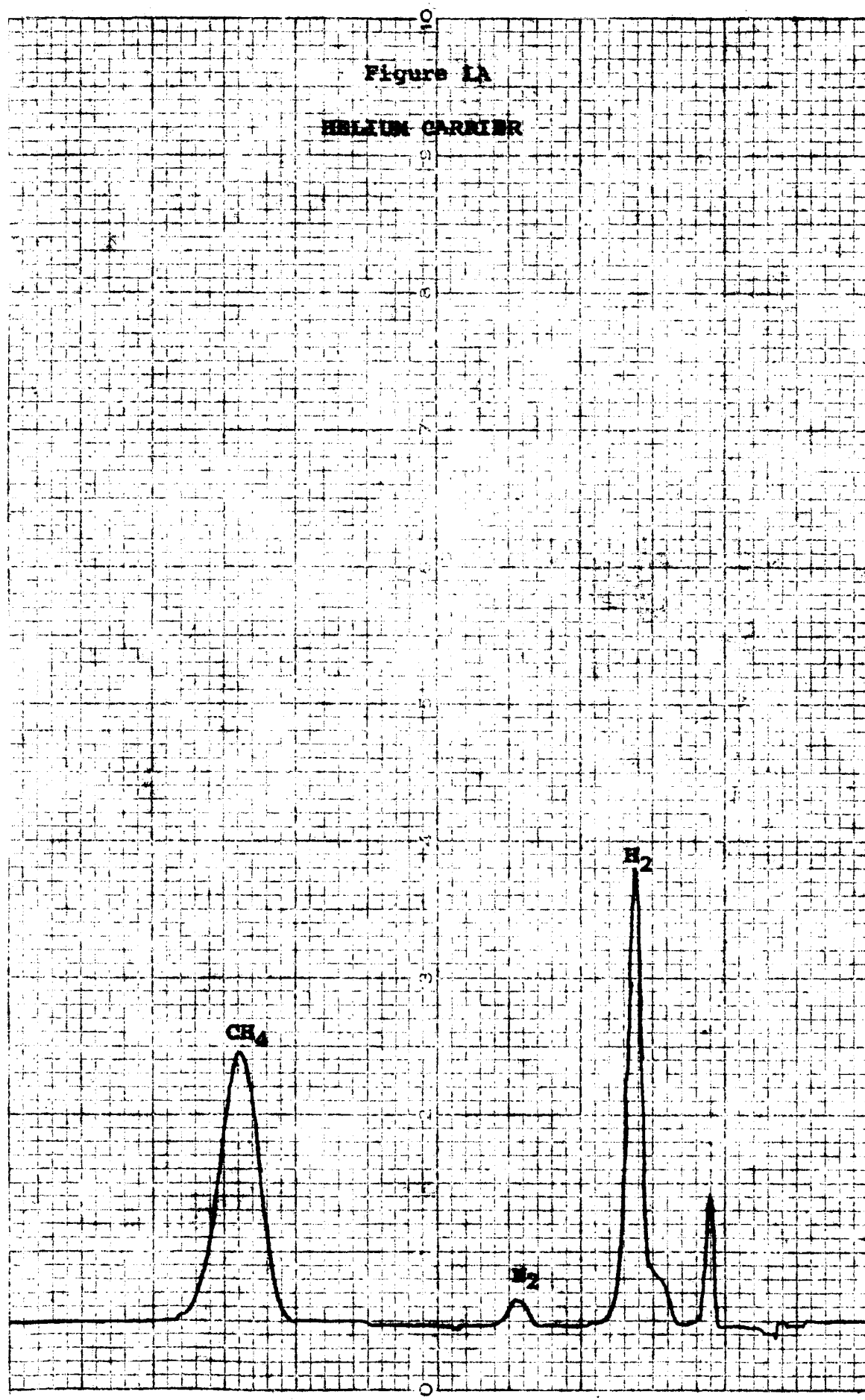
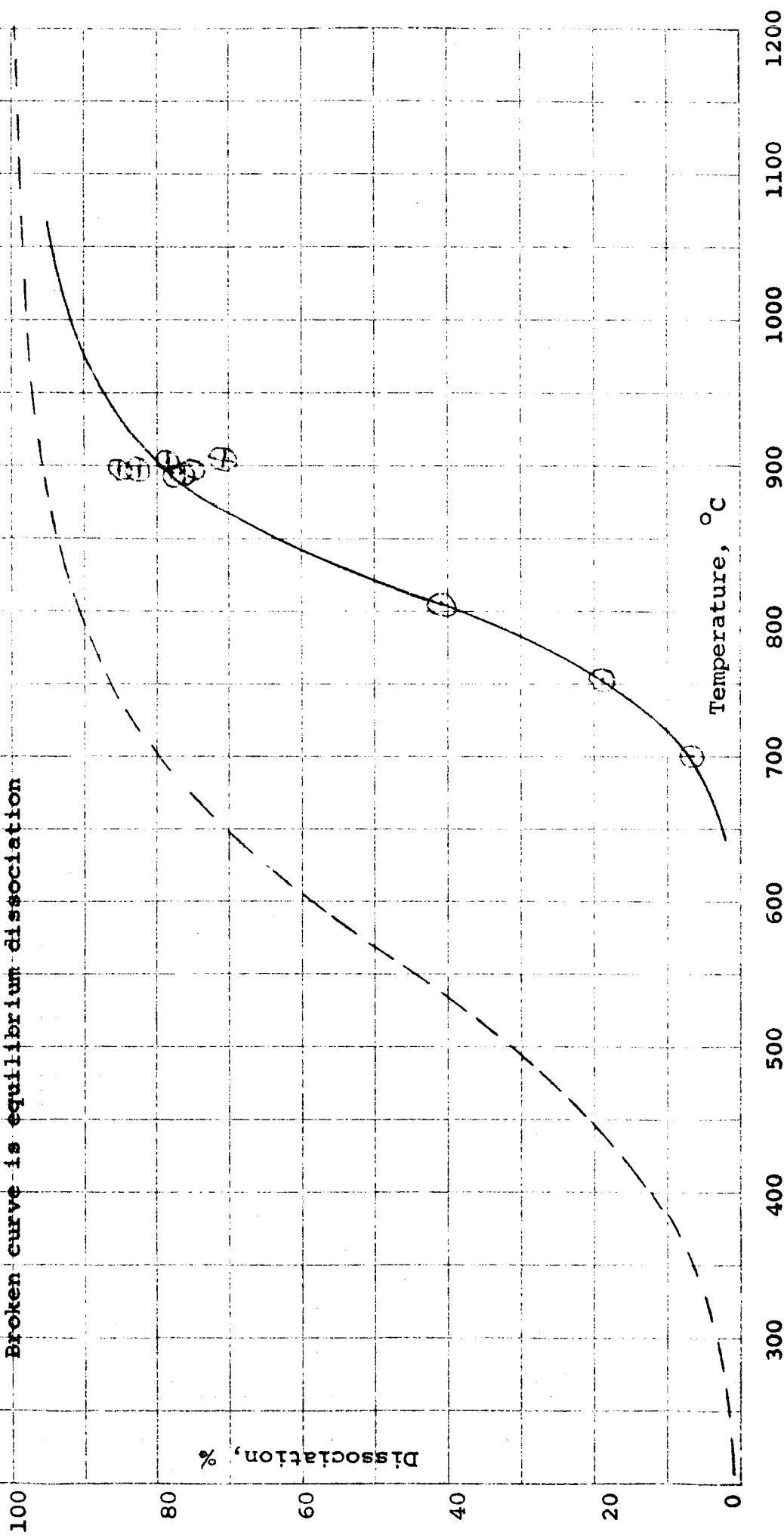


FIGURE 12
PYROLYSIS OF METHANE OVER GIRDLER G-3A CATALYST IN A 1/4 FILLED TUBE

Legend:

- ⊙ 34 V/V/Hr.
- ⊖ 51 V/V/Hr.
- ⊕ 68 V/V/Hr.

Broken curve is equilibrium dissociation





methane was fed. The average conversion to carbon was 27%. Comparison with the results shown in Figure 5 show that at 1000^o C conversion at 1000^o and 33 V/V/hr is comparable with that of cocoanut charcoal after deactivation.

Two other low specific surface carbon packings were evaluated by small furnace experiments. These were arc-light carbon and electrode graphite. These substances were crushed and sized as were the charcoal briquettes. Both runs were made at 50 cc/min feed rate (43 V/V/hr.). The results are plotted in Figure 9. The data correlate well with the curve which fits the open tube data and the granulated charcoal briquette data. It is evident that low specific surface carbon packings do not appreciably increase the dissociation which can be obtained in an open tube at the same temperature and feed rate.

5. Catalytic Pyrolysis. Contact hydrogenation catalysts which are prepared to maintain activity at high temperatures may be expected to promote methane dissociation. We have selected two commercial catalysts of this type for study.

Cyanamid NR-1 Aerocatalyst is a promoted nickel oxide catalyst prepared by American Cyanamid Corp. primarily for reforming methane with steam. Upon reduction this catalyst becomes an active hydrogenation catalyst. The catalyst was in the form of 5/8" rings. These were crushed and sized and about 70 cc of 1/4" to 5/8" granules were mounted between asbestos plugs in a 3/4" Vycor tube which was heated in the small furnace. After purging air out with nitrogen the temperature was slowly raised in a stream of hydrogen. After active reduction was over, as indicated by the absence of water condensate in the off gas,



methane was introduced at 1000°C, 50 cc/min feed rate - (43 V/V/hr.). The data are shown in Figure 10. Initial dissociation was 97-99% but started to fall off after 5 hours on stream. At this time the furnace was shut down, the methane flow stopped, the inlet and outlet tubes blocked, and the apparatus allowed to cool and stand over the weekend. The run was resumed on Monday morning and continued for three hours when increase in back pressure warned that a stoppage was developing. The furnace was allowed to cool, after which the catalyst was removed. The granules had for the most part disintegrated into a black powder. It was possible, however, to return the powder to the furnace and resume operation. The initial activity was still high, but after an hour on stream it started to decline rapidly. The furnace was again cooled, the catalyst removed and recharged. It regained its initial activity only momentarily and then declined sharply. The run was ended when the exit tube plugged with tar.

The results indicate that this catalyst is rather rapidly deactivated by the deposited carbon. The revival of activity observed at hour 5.2 when the reaction was started after the reactor had cooled over a week end may be due to dislodgement of carbon from the catalyst surface by the thermal contraction on cooling. The transitory effect of emptying and recharging the reactor at hour 11.5 is no doubt due to redistribution of the catalyst, bringing into the hot zone some active catalyst which had previously been in the cooler bed ends. The useful life of the catalyst under the test conditions is 10 - 15 hours.

Girdler G-3A catalyst is a chromium promoted iron oxide catalyst prepared by the Chemtron Corporation for service in converting CO and steam to CO₂ and H₂. This catalyst was in the



form of cylindrical pellets, 1/4" diameter and 1/4" long. Preliminary small scale experiments showed that after reduction it promoted the dissociation of methane vigorously. 813 g of catalyst, about 700 cc, were charged into a 1 3/4" "Zircum" refractory tube between asbestos tape plugs. The catalyst was slowly heated in the large furnace in a stream of hydrogen until the temperature rose to 750^o, and was held at that temperature until no more water collected in a water jacketed condenser through which the off hydrogen was passed. The tube was cooled to room temperature and weighed. The weight loss was 225 g, 214 cc of water were condensed out of the off gas. Methane was next introduced at 100 cc/min. At this low flow rate 1.0% conversion was observed at 520^oC. Water formation was observed at 790^oC and 2.7% of CO was found in the off gas, indicating that the reaction $C + H_2O \rightleftharpoons CO + H_2$ was occurring. Water production increased steadily as the temperature rose. Hydrogen treating was again resumed and the temperature increased to 1000^oC, where it was held until water production apparently ended. The run was then continued with methane at 200 cc/min. and 400 cc/min. - (17 and 34 V/V/hr.). A conversion of 0.5% was observed at 560^oC indicating possibly some improvement of the low temperature activity of the catalyst. At 793^o CO was again found in the off gas, but in much lower concentration than before. 94.5% conversion was observed between 880^oC and 900^oC. The data obtained are shown in Figure 11. The run was terminated when the reactor plugged. Because of the water production after the main reduction the weight of carbon produced could not be measured.



Examination of the bed showed that the carbon had been produced in a zone about 11 cm long, about one third of the bed length. The remaining $2/3$ of the bed contained only a little carbon. In the heavily carbonized zone the pellets of catalyst had completely disintegrated. At the zone boundary some pellets were observed still intact but several times their initial size. Carbon evidently forms all through the catalyst mass. However, no loss in activity was observed.

Because of the high activity of the catalyst and its resistance to carbon deactivation, 114 g of the reduced pills taken from the zone where little carbon was formed were recharged. They were distributed along a 30 cm length of the tube so as to fill about one quarter of the volume. Methane flows of 400, 600 and 800 cc/min. were used, (34, 51 and 68 V/V/hr.) based on the volume of the reaction zone. The data from this run are shown in Figure 12. The run was terminated when the bed plugged. Examination showed that again carbon formation was limited to a zone about 11 cm long, about 37% of the bed length. 110 g of carbon were deposited. Thus the contents of the reactor averaged 40% carbon by weight. 724 l of methane passed through the reactor. The average dissociation was 53.8%.

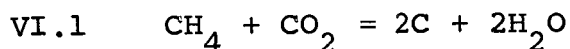
Small amounts of CO were observed in the off gas and 4 cc of water were found in the cold trap. Complete reduction of the catalyst is difficult.

The dissociations are lower than those for the fully packed tube shown in Figure 11. However, the difference is small considering the reduction in catalyst.



VI. REACTION OF METHANE AND CARBON DIOXIDE

In conjunction with the above studies of methane decomposition in the electric arc, the following reaction was also examined:



This reaction was of interest to us, since if it would occur in the arc, then only one-half of the CO_2 removed from a closed environment would have to be converted to methane in the Methoxy system. This volume of methane would then be mixed with an equal volume of CO_2 and the resulting mixture would then be passed into the arc. Water formed from this reaction would be combined with the water obtained in the methanation reaction and electrolyzed. The resulting oxygen would be returned to the closed environment and the hydrogen would be reused in further methanation of CO_2 . Inasmuch as this reaction afforded us a possible route alternate to that presently envisioned, an experiment to determine its feasibility was undertaken.

A 50-50 mixture of CO_2 and CH_4 was passed into the reaction system previously discussed. The flowrate of the mixture was set at 400 cc/min. Molybdenum electrodes, spaced 1/4" apart, were mounted in the reaction flask. These were not rotated since the arc was concentrated by the capacitor. Duration of the run was 40 minutes with 170 watts being supplied to the arc.

The reaction as expressed by equation VI.1 did not occur. There was not visible evidence of carbon or water being formed. Instead, analysis of the exiting gas stream indicated that CO, constituting about 25% of the exit gas stream was being produced. Hydrogen was also present in about an equal amount. Hence, it

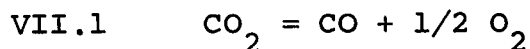


appeared that methane was being partially converted to carbon and hydrogen. CO_2 , on the other hand, apparently formed CO and O_2 . Then, instead of water being formed, the O_2 combined with the carbon and formed more CO. A detailed analysis of the results was not undertaken since there was no direct evidence that the desired reaction had occurred to any extent. Therefore, further study of this particular reaction was abandoned.

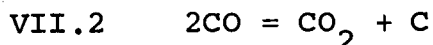


VII. ELECTRIC ARC DECOMPOSITION OF CARBON DIOXIDE

Our second progress report indicated our previous experimental efforts and results when CO₂ was passed through the electric arc. It appeared desirable to us to briefly examine this reaction in the laboratory set-up discussed above to determine if there would be any improvement over the results that had been previously obtained. For purposes of review, the reaction that occurs in the arc can be expressed as follows:



This equation represents the first step in the Carboxy process. The CO produced according to the above reaction is then catalytically converted to CO₂ as indicated in the following equation:



Carbon dioxide, reformed by this reaction, is then recycled into the arc and further converted.

In our second progress report we indicated that the O₂ present in the effluent gas stream amounted to 1.24% by volume. This result was obtained when the inlet flow rate of CO₂ was 800 cc/min. and was equivalent to a 2.48% conversion of the incoming CO₂. This indicates that 19.8 cc of the incoming CO₂ were being converted to CO per minute.

In our present work, pure CO₂ was passed into the reaction tube at 235 cc/min. Two experiments were tried wherein carbon and molybdenum electrodes were used with the distance between electrodes being 1/4". Approximately 165 watts were supplied to the arc with the capacitor connected to the transformer. Inasmuch as there were no short-circuiting problems involved in this work, the electrodes were not rotated.



When the carbon electrodes were used, the composition of the effluent gas stream was $\text{CO} = 10.3\%$, $\text{O}_2 = 5.3\%$ and $\text{CO}_2 = 84.4\%$. Since the carbon electrodes appeared to be eroded by the arc, molybdenum electrodes were used in the second experiment. These were also eroded and there was visible evidence that molybdenum oxides were formed. However, when the latter electrodes were used, an analysis of the exiting gas stream showed the composition to be $\text{CO} = 15.2\%$, $\text{O}_2 = 10.2\%$ and $\text{CO}_2 = 74.6\%$. The oxygen content was double that found in the first experiment. This result indicates that approximately 20% or about 47 cc of the incoming CO_2 was being converted to CO per minute.

There was less oxygen than expected in the gas stream but this was probably due to the fact that some of it was lost in forming molybdenum oxides.

H for equation (VII.1) is + 67,636 calories. This corresponds to a minimum energy input requirement of 2.23 KWH/lb. of O_2 produced. Using this value and calculating from the data of the last experiment, 41.6 KWH/lb. of O_2 were required. Hence the percent efficiency attained was about 5.4. Inasmuch as this represents a marked improvement over the previous results, it is hoped that the efficiency can be increased even further. Further examination of this reaction will be undertaken when improved reaction tubes are designed.



VIII. SUMMARY AND CONCLUSIONS

A. Electric Arc Decomposition of Methane

Results indicate that decomposition of methane in the electric arc yields hydrogen, carbon and acetylene as products. Experiments have shown that if sufficient acetylene is fed into the reactor no net formation of acetylene occurs. Based on these observations and data it appears to be feasible to design a methane decomposition system in which acetylene and undecomposed methane are continually recycled to the reactor with addition of fresh methane and with a net formation of only carbon and hydrogen from the methane. The acetylene would, in effect, act only to suppress the formation of more acetylene.

The problem still remaining is one of collection and disposal of carbon formed in the reactor. Several ideas have been proposed to eliminate the problem of carbon deposition on electrical leads. Solution of this problem should allow the construction of a practical operating model of this reactor which can then be used in conjunction with the catalytic methanation reactor. Perhaps the most promising approach to carbon removal is one in which gas from the reactor is continually sucked through a filter and back into the reactor with no net removal of gas from the reactor but with carbon being removed continuously. Such a system could use two carbon filters in parallel so that one is being cleaned while the other is in use.

B. Pyrolysis of Methane

The results show that methane can be 80 - 90% decomposed at useful flow rates by passage through either an empty tube at 1200°C, or through a tube packed with a low surface granulated



carbon. Over a high surface carbon activated cocoanut charcoal, 97% decomposition was observed at 1000°C but the effect was very short-lived. Over an active iron catalyst, 80-90% dissociation was observed between 850 and 900°C . This catalyst was found to be very resistant to carbon deactivation.

The relative merits of the high temperature non-catalyzed and the lower temperature catalyzed pyrolysis will depend primarily upon how well they can be made the basis of a carbon disposal system. The data presented disclose the conditions under which this system must work. Probably a method must be found continuously to remove carbon from the reactor. The catalyzed pyrolysis can be used successfully only if the amount of catalyst needed is very small. The iron catalyst tested shows some promise in this respect. In addition, nickel and iron deposited on light, fluffy, supports appear to have promising potential.

C. Arc Decomposition of CO_2

Decomposition of CO_2 in the electric arc appears to have shown more promising results than those obtained previously. Proper design of the reaction system may lead to appreciably increased oxygen yields thereby making this process a strong candidate for consideration. Further work along these lines will be carried out.